

THE OVERLAP INTEGRAL IN THE MOLECULAR-ORBITAL THEORY OF CONJUGATED COMPOUNDS*

I. GENERAL THEORY

By I. M. BASSETT† and R. D. BROWN†

[Manuscript received March 22, 1956]

Summary

The simple LCAO molecular-orbital theory with inclusion of overlap is developed in terms of two basic quantities—the atom charge density and the bond charge density. General formulae are derived for these and other related quantities and some identities are obtained for checking numerical calculations.

Certain singularities arising in the mathematics are discussed in Appendix I.

I. INTRODUCTION

The molecular-orbital theory of conjugated compounds has been developed extensively in the approximation wherein the overlap of adjacent atomic orbitals is neglected (Coulson and Longuet-Higgins 1947*a*, 1947*b*, 1948*a*, 1948*b*, 1948*c*) and the application of the results to interpret chemical reactivities (Brown 1952) and molecular geometry (Coulson, Daudel, and Robertson 1951) has been fruitful. However, little attempt has been made to determine how serious is the approximation of neglecting overlap, other than to show (Chirgwin and Coulson 1950) that it is possible in the case of hydrocarbon systems to define quantities such as charge densities q , and bond orders p , such that (i) they are independent of the overlap integral S (subject to the Mulliken approximation, see below), and (ii) when overlap is neglected the use of these quantities in discussions of chemical reactivities can be justified. It is felt that these generalizations are not necessarily those most suited for discussing chemical reactivities when overlap is taken into account and it is proposed now to develop an alternative generalization which appears more satisfactory as a basis of a theory of chemical reactivity.

We shall develop the general theory for conjugated systems in the present paper. In Part II of this series (Bassett and Brown 1956) the particular case of hydrocarbons will be considered and numerical results for various conjugated systems will be considered in a subsequent paper.

II. THE ATOM CHARGE DENSITY

The charge density has played a central role in the theory of chemical reactivities. Its definition represents a mode of partitioning the π -electrons among the atoms of the conjugated framework. Initially (Pauling and Wheland

* These results formed part of a thesis submitted by Mr. I. M. Bassett for the M.Sc. degree at the University of Melbourne, February 1955.

† Department of Chemistry, University of Melbourne.

1935), it was employed under the qualitative supposition that an electrophilic reagent would preferentially attack the position of highest charge, the converse applying for a nucleophilic reagent. In order to put the theory on a more quantitative basis it is necessary to relate q to the activation energy for the particular substitution reaction under consideration. This has been discussed in detail elsewhere (Brown 1952), the underlying assumptions of the correlation being that the approaching electrophilic reagent is imagined to enhance the electronegativity of the atom being attacked, that is, its Coulomb parameter* α_μ is perturbed by the reagent, and that q_μ can be defined as $\partial E / \partial \alpha_\mu$, E being the total π -electron energy of the conjugated system. From the point of view of chemical reactivities then it is appropriate to take for the generalized definition of the atom charge density the relationship

$$a_\mu = \partial E / \partial \alpha_\mu. \quad \dots\dots\dots (1)$$

The symbol a_μ has been employed to distinguish our definition from that of Chirgwin and Coulson (1950). Their definition is most simply expressed in terms of the coefficients of the various molecular orbitals. Thus if the LCAO expression for a molecular orbital φ_j is

$$\varphi_j = \sum_\mu c_{j\mu} \chi_\mu, \quad \dots\dots\dots (2)$$

χ_μ being a $2p\pi$ atomic orbital on atom μ , then the Chirgwin-Coulson definition of q_μ is

$$q_\mu = \sum_j n_j (c_{j\mu} \sum_\nu c_{j\nu} S_{\mu\nu}), \quad \dots\dots\dots (3)$$

n_j being the number of π -electrons present in φ_j , and $S_{\mu\nu}$ the overlap integral between χ_μ and χ_ν .

This definition of electron density was first introduced by Wheland (1942), presumably because it appears to be the most reasonable way of partitioning the π -electrons among the atoms of the conjugated framework in such a way that all the π -electrons are so allocated, that is, so that $\sum_\mu q_\mu = N$, where N is the total number of π -electrons present in the conjugated system. However, this feature is gained at the expense of the simple differential relationship (1). An analogous type of relationship was derived by Chirgwin and Coulson by introducing a mixed tensor for the Hamiltonian which is not in general Hermitian-symmetric so that the physical interpretation of the elements is of dubious validity.

The quantity a_μ , defined in (1), will be shown to satisfy the relationship

$$a_\mu = \sum_j n_j c_{j\mu}^2, \quad \dots\dots\dots (4)$$

with $\sum_\mu a_\mu < N$.† This definition constitutes a partitioning of the π -electrons among the atoms of the conjugated framework, but leaving part of the π -electron

* Coulomb integrals α_μ , resonance integrals $\beta_{\mu\nu}$, and overlap integrals $S_{\mu\nu}$ are fundamental quantities in the molecular-orbital theory. They have been fully described elsewhere (e.g. Brown 1952).

† This inequality can be established for hydrocarbons in their ground states (see Part II of this series) and will apply to many other conjugated systems. It does not apply to highly excited states of conjugated systems but we are primarily concerned with the theory of chemical reactivities of ordinary molecules, that is, molecules in their ground states.

shell not disturbed in this way but distributed over the bonds; a_μ reduces to q_μ when the overlap integrals are all zero. The definition (4) of atom charge density has previously been proposed by McWeeny (1951, 1952), and Mulliken (1932, 1955) has used a similar procedure for dissecting molecular charge distributions.

The advantages of a_μ as compared with q_μ are:

- (i) The simple differential relationship to E (1) is preserved.
- (ii) The formula (4) in terms of the coefficients results in less computational labour than is involved in formula (3).
- (iii) For hydrocarbon systems, or more specifically when all atoms of the framework have equal Coulomb integrals, $c_{j\mu}^2$ for $S_{\mu\nu} \neq 0$, may be simply derived from the corresponding coefficients for $S_{\mu\nu} = 0$ (subject to the Mulliken approximation). Thus if the molecular-orbital energies e_j and the coefficients $c_{j\mu}$ have been calculated ignoring overlap, the calculation of the a_μ is rapidly done. This is considered in more detail below.
- (iv) For alternant hydrocarbons every $a_\mu \neq 1$ in contrast to the general result $q_\mu = 1$. The advantage of this is that the chemical reactivities of alternant hydrocarbons may thus be discussed in terms of the atom charge densities a_μ , which are readily computable, while in the alternative theory recourse must be made to the polarizability coefficients, which involve lengthy calculation when overlap is included.

III. THE BOND CHARGE DENSITY

The bond order p has been used extensively to predict and interpret lengths of aromatic bonds, and a simple function

$$F_\mu = X - \sum_\nu p_{\mu\nu} \quad \dots\dots\dots (5)$$

termed the free valence of atom μ (X is a numerical constant now taken to be $\sqrt{3}$) has been employed in discussions of homolytic chemical reactivities (Coulson 1946; Brown 1952; Burkitt, Coulson, and Longuet-Higgins 1953). The justification of using F_μ as a criterion of homolytic chemical reactivity (Brown 1952) depends on the relationship

$$p_{\mu\nu} = \frac{1}{2} \frac{\partial E}{\partial \beta_{\mu\nu}} \quad \dots\dots\dots (6)$$

It is therefore desirable to preserve this relationship when the concept of bond order is generalized to take orbital overlap into account. Unfortunately, the generalization proposed by Chirgwin and Coulson was not based on invariance of (6) but rather invariance of the numerical values of bond orders for alternant hydrocarbon systems. We shall therefore define a new quantity

$$b_{\mu\nu} = \frac{1}{2} \frac{\partial E}{\partial \beta_{\mu\nu}}, \quad \dots\dots\dots (7)$$

and term it the bond charge density to distinguish it from the $p_{\mu\nu}$ of Chirgwin and Coulson. When $S_{\mu\nu}$ tends to zero $b_{\mu\nu}$ tends, of course, to $p_{\mu\nu}$.

Now, when overlap of adjacent orbitals is included in the theory the molecular-orbital quantities E , a_μ , $b_{\mu\nu}$, etc. are formally functions of three types of independent variable α_λ , $\beta_{\lambda\eta}$, and $S_{\lambda\eta}$. Mulliken (1948) has given reasons for assuming that $S_{\lambda\eta}$ is directly proportional to $\beta_{\lambda\eta}$. We shall adopt this assumption throughout the subsequent analysis, and write

$$S_{\lambda\eta}/S = \beta_{\lambda\eta}/\beta = k_{\lambda\eta}, \quad \dots \dots \dots (8)$$

where S and β are the overlap and resonance integrals of a benzene bond. For the above given definition (7) of $b_{\mu\nu}$ it is understood that the substitution $S_{\mu\nu} = \beta_{\mu\nu}S/\beta$ has been made, so that E is expressed as a function of the α_λ and $\beta_{\lambda\eta}$ only.*

IV. FORMULAE FOR a_μ AND $b_{\mu\nu}$

Formulae for a_μ and $b_{\mu\nu}$ in terms of the molecular-orbital coefficients $c_{j\lambda}$ can be derived in the manner of Coulson and Longuet-Higgins (1947a). When (2) is inserted in the variational expression for the molecular-orbital energy ε we obtain

$$\varepsilon = \frac{\sum_\mu c_\mu^2 \alpha_\mu + 2 \sum_{\mu < \nu} \sum c_\mu c_\nu \beta_{\mu\nu}}{\sum_\mu c_\mu^2 + 2 \sum_{\mu < \nu} \sum c_\mu c_\nu S_{\mu\nu}}, \quad \dots \dots \dots (9)$$

and the coefficients c_λ in (9) are determined from the equations

$$\partial \varepsilon / \partial c_\mu = 0, \quad \mu = 1, 2, \dots, M, \quad \dots \dots \dots (10)$$

$$\sum_\mu c_\mu^2 + 2 \sum_{\mu < \nu} \sum c_\mu c_\nu S_{\mu\nu} = 1. \quad \dots \dots \dots (11)$$

In equation (10), M is the number of atoms comprising the conjugated system. In the differentiations in (10), ε is regarded as a function of the α_λ , the $\beta_{\lambda\eta}$, the $S_{\lambda\eta}$, and the c_λ , and the symbol ε will be used to represent the orbital energy when regarded as a function of these variables. The energy of the j th molecular orbital may also be expressed as a function of the α_λ and $\beta_{\lambda\eta}$ alone by expressing the j th solution of equations (10) and (11), namely, $c_{j1}, c_{j2}, \dots, c_{jM}$, in terms of the α_λ , $\beta_{\lambda\eta}$, and $S_{\lambda\eta}$, and then by making the Mulliken substitution $S_{\lambda\eta} = \beta_{\lambda\eta}S/\beta$. When the orbital energy is regarded as a function of the α_λ and the $\beta_{\lambda\eta}$ only, we shall use for it the symbol e , and for the energy of the j th molecular orbital the symbol e_j .

Thus

$$\begin{aligned} \partial e_j / \partial \alpha_\mu &= \partial \varepsilon_j / \partial \alpha_\mu + \sum_\nu \frac{\partial \varepsilon_j}{\partial c_\nu} \frac{\partial c_\nu}{\partial \alpha_\mu} \\ &= \partial \varepsilon_j / \partial \alpha_\mu \quad \dots \dots \quad (\text{from (10) and (11)}) \\ &= e_{j\mu}^2 \quad \dots \dots \dots (12) \end{aligned}$$

* McWeeny (1951, 1952) and Mulliken (1955) have used different definitions of bond charges in which the variation of $S_{\mu\nu}$ proportionally to $\beta_{\mu\nu}$ is not taken into account. Their definitions are given in terms of the molecular-orbital coefficients and are most conveniently compared with equation (18) of the present paper.

The total π -electron energy is

$$E = \sum_j n_j e_j, \quad (13)$$

so that

$$a_\mu = \sum_j n_j c_{j\mu}^2. \quad (14)$$

Similarly,

$$\begin{aligned} \frac{\partial e_j}{\partial \beta_{\mu\nu}} &= \frac{\partial \varepsilon_j}{\partial \beta_{\mu\nu}} + \beta \frac{\partial \varepsilon_j}{\partial S_{\mu\nu}} + \sum_\nu \frac{\partial \varepsilon_j}{\partial c_\nu} \frac{\partial c_\nu}{\partial \beta_{\mu\nu}} \\ &= \frac{\partial \varepsilon_j}{\partial \beta_{\mu\nu}} + \beta \frac{\partial \varepsilon_j}{\partial S_{\mu\nu}} \\ &= 2c_{j\mu}c_{j\nu}(1 - e_j S/\beta). \end{aligned} \quad (15)$$

If we now use the transformations of Wheland (1942)

$$(\alpha - e)/(\beta - Se) = x, \quad (16)$$

and of Mulliken and Rieke (1941)

$$\gamma = \beta - S\alpha, \quad (17)$$

then from (7), (13), and (15)

$$b_{\mu\nu} = \delta \sum_j n_j c_{j\mu} c_{j\nu} / (1 - Sx_j), \quad (18)$$

where

$$\delta = \gamma/\beta. \quad (19)$$

To obtain contour integral formulae for a_μ and $b_{\mu\nu}$ we start with the secular determinant $\Delta(e)$, which is obtained from the secular equations (10). If we express the Coulomb integral of the μ th atom α_μ , as

$$\alpha_\mu = \alpha + h_\mu \gamma, \quad (20)$$

where α is the standard Coulomb integral of a carbon atom in benzene, then division of each row of $\Delta(e)$ by $\beta - Se$ gives a new determinant $D(x)$ in which the μ th diagonal element is $(1 - Sh_\mu)x + h_\mu$ and the off-diagonal elements, from (8), are $k_{\mu\nu}$.

From the definition (16) of x ,

$$e = (\alpha - \beta x)/(1 - Sx), \quad (21)$$

$$de/dx = -\gamma/(1 - Sx)^2. \quad (22)$$

Now, x is a function of h_μ and $k_{\mu\nu}$, and

$$\partial x / \partial h_\mu = - \frac{\partial D}{\partial h_\mu} \bigg/ \frac{\partial D}{\partial x} = -(1 - Sx) D_{\mu,\mu} / D', \quad (23)$$

where $D_{\mu,\mu}$ is obtained from D by omitting row μ and column μ , and the prime denotes differentiation with respect to x .

Hence from (20), (22), and (23)

$$\begin{aligned} \partial e_j / \partial \alpha_\mu &= (\partial e_j / \partial h_\mu) (dh_\mu / d\alpha_\mu) \\ &= (de/dx) (\partial x / \partial h_\mu) (1/\gamma) \\ &= D_{\mu,\mu} / (1 - Sx_j) D', \end{aligned} \quad (24)$$

and, from (1)

$$a_{\mu} = \sum_j \frac{n_j D_{\mu,\mu}}{(1 - Sx_j) D'} \quad (25)$$

This formula for a_{μ} is particularly convenient for computational purposes if one wishes to consider only one atom in a large conjugated system (cf. Brown 1956)

Again

$$\partial x / \partial k_{\mu\nu} = 2(-1)^{\mu+\nu+1} D_{\mu,\nu} / D', \quad (26)$$

$$\begin{aligned} \partial e / \partial \beta_{\mu\nu} &= (de/dx)(\partial x / \partial k_{\mu\nu})(dk_{\mu\nu}/d\beta_{\mu\nu}) \\ &= 2\delta(-1)^{\mu+\nu} D_{\mu,\nu} / D'(1 - Sx)^2, \end{aligned} \quad (27)$$

and

$$b_{\mu\nu} = \delta \sum_j \frac{n_j (-1)^{\mu+\nu} D_{\mu,\nu}}{(1 - Sx_j)^2 D'} \quad (28)$$

Similarly, this formula for $b_{\mu\nu}$ is useful for obtaining the numerical value for just one or two bonds in a large molecule.

Contour integral formulae for a_{μ} and $b_{\mu\nu}$ may readily be derived from (25) and (28). We have, assuming that all occupied molecular orbitals hold two π -electrons, as is normally the case

$$a_{\mu} = \frac{1}{\pi i} \oint_{\Gamma} \frac{D_{\mu,\mu}(x)}{(1 - Sx)D(x)} dx, \quad (29)$$

$$b_{\mu\nu} = \frac{(-1)^{\mu+\nu}\delta}{\pi i} \oint_{\Gamma} \frac{D_{\mu,\nu}(x)}{(1 - Sx)^2 D(x)} dx, \quad (30)$$

where x is regarded as a complex variable and the contour Γ includes just those zeros of $D(x)$ which correspond to occupied orbitals. For nearly all conjugated systems these zeros are real and negative, all other zeros being real and positive, and Γ may conveniently be taken to be the imaginary axis plus a semicircular arc of unbounded radius on the left side of the imaginary axis (cf. Coulson and Longuet-Higgins 1947a). Since the modulae of the integrands in (29) and (30) for large $|x|$ are $O(1/|x|^2)$ and $O(1/|x|^4)$ respectively, the contour integrals for a_{μ} and $b_{\mu\nu}$ may be reduced to

$$a_{\mu} = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{D_{\mu,\mu}(ix)}{(1 - iSx)D(ix)} dx, \quad (31)$$

$$b_{\mu\nu} = \frac{(-1)^{\mu+\nu}\delta}{\pi} \int_{-\infty}^{\infty} \frac{D_{\mu,\nu}(ix)}{(1 - iSx)^2 D(ix)} dx. \quad (32)$$

These formulae for a_{μ} and $b_{\mu\nu}$ may be evaluated by the method described by Coulson (1940) and are most convenient if the zeros of the molecular secular determinant are not known and just one or two of the a_{μ} or $b_{\mu\nu}$ are required. (When the complete set of a_{μ} and $b_{\mu\nu}$ are needed, formulae (4) and (18) are best suited to the numerical work.)

V. POLARIZABILITIES

In the simple theory in which overlap is neglected, quantities termed atom-atom polarizabilities, atom-bond polarizabilities, and bond-bond polarizabilities have found many applications (Coulson and Longuet-Higgins 1948b; Longuet-Higgins and Coulson 1949). These polarizabilities are simply the derivatives of q_{μ} and $p_{\mu\nu}$ with respect to α_{λ} and $\beta_{\lambda\gamma}$. We now consider the corresponding derivatives of a_{μ} and $b_{\mu\nu}$.

From equation (29)

$$\frac{\partial a_{\mu}}{\partial h_{\nu}} = \frac{1}{\pi i} \oint_{\Gamma} \frac{\partial}{\partial h_{\nu}} \left(\frac{D_{\mu,\mu}}{(1-Sx)D} \right) dx, \quad \dots \quad (33)$$

and*

$$\begin{aligned} \frac{\partial}{\partial h_{\nu}} \left(\frac{D_{\mu,\mu}}{(1-Sx)D} \right) &= \frac{(1-Sx)DD_{\mu\nu,\mu\nu}(1-Sx) - D_{\mu,\mu}(1-Sx)^2 D_{\nu,\nu}}{(1-Sx)^2 D^2} \\ &= (DD_{\mu\nu,\mu\nu} - D_{\mu,\mu}D_{\nu,\nu})/D^2. \quad \dots \quad (34) \end{aligned}$$

From Jacobi's theorem of adjugates

$$DD_{\mu\nu,\mu\nu} = D_{\mu,\mu}D_{\nu,\nu} - D_{\mu,\nu}D_{\nu,\mu},$$

so that

$$\frac{\partial}{\partial h_{\nu}} \left(\frac{D_{\mu,\mu}}{(1-Sx)D} \right) = -D_{\mu,\nu}^2/D^2, \quad \dots \quad (35)$$

and

$$\partial a_{\mu}/\partial \alpha_{\nu} = \frac{1}{\gamma \pi i} \oint_{\Gamma} -\frac{D_{\mu,\nu}^2}{D^2} dx. \quad \dots \quad (36)$$

Similarly, from equation (30),

$$\frac{\partial b_{\mu\nu}}{\partial h_{\lambda}} = 2\delta \frac{(-1)^{\mu+\nu}}{\pi i} \oint_{\Gamma} \frac{\partial}{\partial h_{\lambda}} \left(\frac{D_{\mu,\nu}}{(1-Sx)^2 D} \right) dx, \quad \dots \quad (37)$$

and

$$\frac{\partial}{\partial h_{\lambda}} \left(\frac{D_{\mu,\nu}}{(1-Sx)^2 D} \right) = \frac{DD_{\lambda\mu,\lambda\nu} - D_{\mu,\nu}D_{\lambda,\lambda}}{(1-Sx)^2 D^2}. \quad \dots \quad (38)$$

Again, we use Jacobi's theorem to obtain

$$DD_{\lambda\mu,\lambda\nu} - D_{\mu,\nu}D_{\lambda,\lambda} = -D_{\mu,\lambda}D_{\lambda,\nu},$$

hence

$$\frac{\partial b_{\mu\nu}}{\partial \alpha_{\lambda}} = \frac{2}{\beta} \frac{(-1)^{\mu+\nu+1}}{\pi i} \oint_{\Gamma} \frac{D_{\lambda,\mu}D_{\lambda,\nu}}{(1-Sx)^2 D^2} dx. \quad \dots \quad (39)$$

Now, from the definitions (1) and (7) of a_{μ} and $b_{\mu\nu}$, we have

$$\partial a_{\mu}/\partial \beta_{\lambda\gamma} = 2\partial b_{\lambda\gamma}/\partial \alpha_{\mu}, \quad \dots \quad (40)$$

* It is convenient to use the symbol $D_{\alpha\beta,\gamma\delta}$ to represent the determinant derived from D by striking out rows α and β and columns γ and δ .

and, therefore, it remains to obtain $\partial b_{\mu\nu}/\partial\beta_{\lambda\eta}$. We proceed as before :

$$\frac{\partial}{\partial k_{\lambda\eta}} \left(\frac{D_{\mu,\nu}}{(1-Sx)^2 D} \right) = \frac{(-1)^{\lambda+\eta}}{(1-Sx)^2 D^2} \{ D(D_{\lambda,\mu} D_{\eta,\nu} + D_{\eta,\mu} D_{\lambda,\nu}) - 2D_{\mu,\nu} D_{\lambda,\eta} \}. \quad (41)$$

Jacobi's theorem gives

$$\begin{aligned} DD_{\lambda,\mu} D_{\eta,\nu} - D_{\mu,\nu} D_{\lambda,\eta} &= -D_{\mu,\eta} D_{\lambda,\nu}, \\ DD_{\eta,\mu} D_{\lambda,\nu} - D_{\lambda,\eta} D_{\mu,\nu} &= -D_{\mu,\lambda} D_{\eta,\nu}, \end{aligned}$$

therefore

$$\begin{aligned} \frac{\partial}{\partial k_{\lambda\eta}} \left(\frac{D_{\mu,\nu}}{(1-Sx)^2 D} \right) &= \frac{(-1)^{\lambda+\eta+1}}{(1-Sx)^2 D^2} (D_{\mu,\eta} D_{\lambda,\nu} + D_{\mu,\lambda} D_{\eta,\nu}) \\ &= \frac{(-1)^{\lambda+\eta+1}}{(1-Sx)^2 D^2} (D_{\lambda,\mu} D_{\eta,\nu} + D_{\eta,\mu} D_{\lambda,\nu}), \quad \dots \quad (42) \end{aligned}$$

and

$$\partial b_{\mu\nu}/\partial\beta_{\lambda\eta} = \frac{2}{\beta} \frac{(-1)^{\mu+\nu+\lambda+\eta+1}}{\pi i} \oint_{\Gamma} \frac{D_{\lambda,\mu} D_{\eta,\nu} + D_{\eta,\mu} D_{\lambda,\nu}}{(1-Sx)^2 D^2} dx. \quad (43)$$

These contour integrals in equations (37), (39), and (43) may be expressed as real integrals in the way indicated for the integrals in equations (29) and (30).

Alternatively, we may obtain residue formulae analogous to (25) and (28) for the polarizabilities. From equation (36), we have

$$\partial a_{\mu}/\partial\alpha_{\nu} = -\frac{1}{Y} \sum_j n_j R_j, \quad \dots \quad (44)$$

where (Brown 1956)

$$R_j = \frac{d}{dx} \left[\frac{D_{\mu,\nu}^2(x)}{F_j^2(x)} \right]_{x=x_j},$$

and

$$D(x) = (x - x_j) F_j(x).$$

Thus

$$R_j = \frac{2D_{\mu,\nu}(x_j)}{F_j^3(x_j)} \{ F_j(x_j) D'_{\mu,\nu}(x_j) - F'_j(x_j) D_{\mu,\nu}(x_j) \}, \quad \dots \quad (45)$$

and

$$\begin{aligned} F_j(x_j) &= D'(x_j), \\ 2F'_j(x_j) &= D''(x_j), \end{aligned}$$

so that we find after substituting in (45) and (44)

$$\frac{\partial a_{\mu}}{\partial\alpha_{\nu}} = \frac{1}{Y} \sum_j \frac{n_j D_{\mu,\nu}(x_j)}{D'^3(x_j)} \{ D''(x_j) D_{\mu,\nu}(x_j) - 2D'(x_j) D'_{\mu,\nu}(x_j) \}. \quad (46)$$

This formula is particularly convenient for calculations of polarizabilities when the energy parameters x_j for the occupied orbitals have been calculated, since in the course of the calculation, if Newton's method has been employed in finding the zeros of D , then the values of $D'(x_j)$ will already be known.

Similarly, it is possible to obtain expressions for $\partial\alpha_\mu/\partial\beta_{\lambda\eta}$ and $\partial b_{\mu\nu}/\partial\beta_{\lambda\eta}$ from equations (39) and (43) respectively. However, the formulae become unwieldy. It will be shown elsewhere (Bassett and Brown unpublished data), that it is simpler to obtain $\partial c_{j\mu}/\partial\alpha_\nu$ and $\partial c_{j\mu}/\partial\beta_{\nu\lambda}$ by differentiation of the secular equations (10) and (11) and numerical solution of the resultant inhomogeneous equations. The values are then inserted into the equations obtained from (14) and (18) by differentiating with respect to α_ν or $\beta_{\lambda\eta}$.

VI. IDENTITIES

We shall now derive some equations which are useful for checking results of numerical calculations of quantities dealt with in the present paper.

Consider the quantity $\Sigma_\mu z_\mu a_\mu$, where z_μ is defined as

$$z_\mu = 1 - S h_\mu. \quad (47)$$

From equation (29)

$$\begin{aligned}\Sigma_\mu z_\mu a_\mu &= \frac{1}{2\pi i} \oint_{\Gamma} \frac{2\Sigma_\mu z_\mu D_{\mu,\mu}(x)}{(1-Sx)D(x)} dx \\ &= \frac{1}{2\pi i} \oint_{\Gamma} \frac{2D'(x)}{(1-Sx)D(x)} dx,\end{aligned}$$

$D'(x)$ representing the derivative of D with respect to x . Thus

$$\Sigma_\mu z_\mu a_\mu = \Sigma_j n_j / (1 - S x_j), \quad (48)$$

and this equation may be used for checking values of a_μ . In addition

$$\begin{aligned}e_j &= (\alpha - \beta x_j) / (1 - S x_j) \\ &= \beta / S - \gamma / S (1 - S x_j),\end{aligned}$$

hence

$$\begin{aligned}E &= \Sigma_j n_j (\alpha - \beta x_j) / (1 - S x_j) \\ &= N \beta / S - \frac{\gamma}{S} \Sigma_j n_j / (1 - S x_j),\end{aligned}$$

and from equation (48)

$$E = N \alpha + \frac{\gamma}{S} (N - \Sigma_\mu z_\mu a_\mu). \quad (49)$$

This equation is particularly convenient for checking calculated values of the a_μ against the calculated total energy E . It is of interest that although the apparently analogous equation in the theory with $S=0$ (Coulson and Longuet-Higgins 1947a, eqn. (74)) contains both charge densities and bond orders, only the a_μ appear in (49), not the $b_{\mu\nu}$. However, it is clearly not possible to derive the Coulson and Longuet-Higgins equation merely by allowing $S \rightarrow 0$ in (49).

VII. REFERENCES

- BASSETT, I. M., and BROWN, R. D. (1956).—*Aust. J. Chem.* **9**: 315.
 BROWN, R. D. (1952).—*Quart. Rev.* **6**: 63.
 BROWN, R. D. (1956).—*J. Chem. Soc.* **1956**: 767.
 BURKITT, F. H., COULSON, C. A., and LONGUET-HIGGINS, H. C. (1951).—*Trans. Faraday Soc.* **47**: 553.

- CHIRGWIN, B. H., and COULSON, C. A. (1950).—*Proc. Roy. Soc. A* **201** : 196.
 COULSON, C. A. (1940).—*Proc. Camb. Phil. Soc.* **36** : 201.
 COULSON, C. A. (1946).—*Trans. Faraday Soc.* **42** : 106.
 COULSON, C. A., DAUDEL, R., and ROBERTSON, J. M. (1951).—*Proc. Roy. Soc. A* **207** : 306.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1947a).—*Proc. Roy. Soc. A* **191** : 39.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1947b).—*Proc. Roy. Soc. A* **192** : 16.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1948a).—*Proc. Roy. Soc. A* **193** : 447.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1948b).—*Proc. Roy. Soc. A* **193** : 456.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1948c).—*Proc. Roy. Soc. A* **195** : 188.
 LONGUET-HIGGINS, H. C., and COULSON, C. A. (1949).—*J. Chem. Soc.* **1949** : 971.
 McWEENY, R. (1951).—*J. Chem. Phys.* **19** : 1614.
 McWEENY, R. (1952).—*J. Chem. Phys.* **20** : 920.
 MULLIKEN, R. S. (1932).—*Phys. Rev.* **41** : 66.
 MULLIKEN, R. S. (1948).—*J. Chim. Phys.* **46** : 497.
 MULLIKEN, R. S. (1955).—*J. Chem. Phys.* **23** : 1833.
 MULLIKEN, R. S., and RIEKE, C. A. (1941).—*J. Amer. Chem. Soc.* **63** : 1770.
 PAULING, L., and WHEELAND, G. W. (1935).—*J. Amer. Chem. Soc.* **57** : 2086.
 WHEELAND, G. W. (1942).—*J. Amer. Chem. Soc.* **64** : 900.

APPENDIX I

The atom charge density a_μ reduces to q_μ for $S=0$, but formula (31) for a_μ does not reduce to the corresponding formula (38) of Coulson and Longuet-Higgins (1947a) at $S=0$. The reason for this is that S is assumed non-zero in the proof of (31) since only for non-zero S is the integrand $O(1/|x|^2)$ for large $|x|$, and so only for non-zero S does the integral around the infinite semicircle vanish. In the course of the proof of (31), a_μ is expressed as a sum of two integrals, one along the semicircle of radius R about the origin in the left half-plane, and the other along the imaginary axis from $-R$ to R . For a given value of S , whether zero or not, both integrals tend to limits as $R \rightarrow \infty$. Both limits have jump discontinuities at $S=0$. Since their sum is continuous at $S=0$ (being equal to a_μ , which is continuous) the discontinuities must be equal and opposite, as can readily be shown analytically. The proof will not be given here as it is straightforward but lengthy.

APPENDIX II

It will be observed that many of the equations in the present treatment have singularities when $x=1/S$, and for x greater than this value one can derive some physically unacceptable results (e.g. an un-normalizable molecular orbital and apparent negative contributions to a_μ). However, the theory is meaningless for $x \geq 1/S$, because the entire range of molecular-orbital energies is spanned, according to (16), as x runs from $-\infty$ to $+1/S$ (the corresponding energies run from $\alpha + \gamma/S$ to $-\infty\gamma$, α and γ both being negative, and S positive). It is possible to obtain values of $x_j \geq 1$ from some secular equations, so that for $S(S < 1)$ sufficiently large such orbitals would be physically meaningless. In such cases fewer than M molecular orbitals may be represented in terms of atomic valence orbitals. To study more excited orbitals some alternative quantum-mechanical representation must be employed.

THE OVERLAP INTEGRAL IN THE MOLECULAR-ORBITAL THEORY OF CONJUGATED COMPOUNDS*

II. HYDROCARBONS

By I. M. BASSETT† and R. D. BROWN†

[Manuscript received April 5, 1956]

Summary

Certain simplifications to the general molecular-orbital theory with inclusion of overlap, developed in Part I of this series, arise when it is applied to hydrocarbon systems. The simpler formulae for atom and bond charges and for polarizabilities are presented, together with some inequalities and identities which apply to hydrocarbon systems.

The law of alternating polarity for the atom charge density is established for alternant conjugated systems.

I. INTRODUCTION

In Part I of this series (Bassett and Brown 1956), a general molecular-orbital theory including overlap was developed for conjugated systems in terms of quantities a_μ and $b_{\mu\nu}$, called respectively the atom charge density of the μ th atom and the bond charge density of the bond between atoms μ and ν . Many of the formulae developed in Part I simplify if the conjugated compound is a hydrocarbon, that is, if all $h_\mu = 0$.‡ We shall represent the molecular-orbital coefficients obtained by neglecting overlap by $c_{j\mu}^0$ and, in general, the superscript zero will be used to denote quantities obtained with the assumption $S=0$.

II. FORMULAE FOR THE COEFFICIENTS

The elements of the secular determinant D for a hydrocarbon are

$$D_{\mu\nu} = \delta_{\mu\nu}x + (1 - \delta_{\mu\nu})k_{\mu\nu},$$

where $\delta_{\mu\nu}$ is the "Kronecker δ ". These are identical with the corresponding elements of D^0 . Now it has been shown (Brown 1956; cf. Coulson and Longuet-Higgins 1947a) that

$$c_{j\mu}^{0\ 2} = D_{\mu,\mu}^0(x_j^0)/D^{0'}(x_j^0), \quad \dots\dots\dots (1)$$

and we have

$$D(x) \equiv D^0(x), \quad \dots\dots\dots (2)$$

hence

$$x_j = x_j^0, \quad \dots\dots\dots (3)$$

* See footnote to Part I of this series, p. 305.

† Department of Chemistry, University of Melbourne.

‡ The symbolism throughout the present paper is that introduced in Part I of this series (see p. 305).

so that

$$c_{j\mu}^{0s} = D_{\mu,\mu}(x_j)/D'(x_j). \quad (4)$$

It was shown in Part I of this series, equations (12) and (24), that

$$\partial c_j / \partial \alpha_\mu = c_{j\mu}^2 = D_{\mu,\mu} / (1 - Sx_j) D', \quad (5)$$

and on inserting (4) into (5) we have

$$c_{j\mu}^2 = c_{j\mu}^{0s}{}^2 / (1 - Sx_j). \quad (6)$$

Formulae (5) and (6) break down if $x_j > 1/S$ (see Part I, Appendix II). However, for hydrocarbons it can be shown (Coulson 1949) that $-3 < x_j < 3$, so that if the customary value of 0.25 is used for S these two formulae are always valid.

III. FORMULAE FOR a_μ AND $b_{\mu\nu}$

The atom charge density a_μ is expressed (Part I, eqn. (4)) in terms of the coefficients as

$$a_\mu = \sum_j n_j c_{j\mu}^2. \quad (7)$$

If we insert (6) in (7), we have

$$a_\mu = \sum_j n_j c_{j\mu}^{0s} / (1 - Sx_j). \quad (8)$$

Since values of x_j and $c_{j\mu}^0$ have been calculated already for many hydrocarbons, equation (8) is usually convenient for computing a_μ .

The corresponding formula for the bond charge density is (Part I, eqn. (18))

$$b_{\mu\nu} = \delta \sum_j n_j c_{j\mu} c_{j\nu} / (1 - Sx_j), \quad (9)$$

and from equation (6) this becomes

$$b_{\mu\nu} = \delta \sum_j n_j c_{j\mu}^0 c_{j\nu}^0 / (1 - Sx_j)^2. \quad (10)$$

IV. FORMULAE FOR POLARIZABILITIES

From equation (2) and the formula for polarizabilities given in Part I (eqn. (36) or (46)) it is clear that

$$\gamma(\partial a_\mu / \partial \alpha_\nu) = \beta(\partial q_\mu^0 / \partial \alpha_\nu). \quad (11)$$

We may therefore obtain a formula for $\partial a_\mu / \partial \alpha_\nu$ in terms of the molecular-orbital coefficients from the formula of this kind for $\partial q_\mu^0 / \partial \alpha_\nu$ given by Coulson and Longuet-Higgins (1947a)

$$\beta(\partial q_\mu^0 / \partial \alpha_\nu) = 4 \sum_{j=1}^{M/2} \sum_{k=M/2+1}^M c_{j\mu}^0 c_{j\nu}^0 c_{k\mu}^0 c_{k\nu}^0 / (x_k - x_j), \quad (12)$$

where there are M atomic orbitals (M even) comprising the conjugated system. Thus from (6), (11), and (12)

$$\gamma(\partial a_\mu / \partial \alpha_\nu) = 4 \sum_j \sum_k (1 - Sx_j)(1 - Sx_k) c_{j\mu} c_{j\nu} c_{k\mu} c_{k\nu} / (x_k - x_j). \quad (13)$$

This formula breaks down if any x_j is greater than $1/S$ but, as pointed out above, this will not arise when the conventional value is used for S .

When the hydrocarbon is an alternant, that is, when the atoms of the conjugated system can be divided into two sets, all neighbours of a member of one set belonging to the other set, formulae (12) and (13) can be transformed into summations over only occupied molecular orbitals (see Coulson and Longuet-Higgins 1947b).

V. LAW OF ALTERNATING POLARITY

The law of alternating polarity may be stated (cf. Coulson and Longuet-Higgins 1947b) in the form: when a heteroatom is substituted for a carbon atom of a conjugated hydrocarbon system the remaining carbon atoms alternately have their charges decreased and increased as we move away from the heteroatom. This principle clearly is confined to systems in which this alternation process is unambiguous, that is, to alternant systems.

The law is established if $\partial a_\mu / \partial \alpha_\nu$ alternates in sign as we consider successive carbon atoms μ , going out from the site of the introduced heteroatom ν . For hydrocarbons, from (11), this amounts to showing that $\partial q_\mu^0 / \partial \alpha_\nu$ alternates in sign and this has been established for alternant hydrocarbons by Coulson and Longuet-Higgins (1947b). Hence, the law of alternating polarity applies to changes in the atom charge densities produced by introduction of a heteroatom.

VI. INEQUALITIES AND IDENTITIES

When overlap is neglected

$$q_\mu^0 = \sum_j n_j c_{j\mu}^0{}^2,$$

hence, provided $x_j < 0$ for all occupied orbitals, as is usually the case,

$$q_\mu^0 < \sum_j n_j c_{j\mu}^0{}^2 / (1 - Sx_j) < a_\mu. \quad (14)$$

Since $\sum_\mu q_\mu^0 = N$, the total number of π -electrons, we have

$$\sum_\mu a_\mu < N, \quad (15)$$

showing that if a_μ is taken to be a measure of the electronic charge on atom μ then part of the total charge is not to be associated with atoms and, therefore, is located in the bonds.

For alternant hydrocarbons every $q_\mu^0 = 1$, so that

$$a_\mu < 1, \quad (16)$$

for such systems.

For hydrocarbons, the identity (49) of Part I reduces to

$$E = N\alpha + \gamma(N - \sum_\mu a_\mu)/S. \quad (17)$$

Furthermore, we can now obtain an identity useful for checking numerical values of $b_{\mu\nu}$. We have

$$c_j^0 = \alpha - x_j \beta = \sum_\mu c_{j\mu}^0{}^2 \alpha_\mu + 2 \sum_{\mu < \nu} c_{j\mu}^0 c_{j\nu}^0 \beta_{\mu\nu},$$

and since for hydrocarbons, all α_μ have the standard value α and we take $\beta_{\mu\nu}$ to be zero when μ and ν are not neighbours, and β when μ and ν are neighbours,

$$e_j^0 = \alpha + 2 \sum_{\text{bonds}} c_{j\mu}^0 c_{j\nu}^0 \beta,$$

where \sum_{bonds} means summation over all bonds of the conjugated system. Thus

$$x_j^0 = -2 \sum_{\text{bonds}} c_{j\mu}^0 c_{j\nu}^0. \quad \dots\dots\dots (18)$$

From (3), (6), and (18)

$$x_j = -2(1 - Sx_j) \sum_{\text{bonds}} c_{j\mu} c_{j\nu},$$

hence

$$\begin{aligned} \sum_{\text{bonds}} b_{\mu\nu} &= \frac{\delta}{2} \sum_{\text{bonds}} \sum_j n_j c_{j\mu} c_{j\nu} / (1 - Sx_j) \\ &= -\frac{\delta}{2} \sum_j n_j x_j / (1 - Sx_j)^2, \quad \dots\dots\dots (19) \end{aligned}$$

and this is a convenient formula for verifying numerical values of $b_{\mu\nu}$ in terms of the orbital energy parameters x_j .

VII. REFERENCES

- BASSETT, I. M., and BROWN, R. D. (1956).—*Aust. J. Chem.* **9**: 305.
 BROWN, R. D. (1956).—*J. Chem. Soc.* **1956**: 767.
 COULSON, C. A. (1949).—*Proc. Camb. Phil. Soc.* **46**: 202.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1947a).—*Proc. Roy. Soc. A* **191**: 39.
 COULSON, C. A., and LONGUET-HIGGINS, H. C. (1947b).—*Proc. Roy. Soc. A* **192**: 16.

THE SPECTRA AND EQUILIBRIA OF NITROSONIUM ION, NITROACIDIUM ION, AND NITROUS ACID IN SOLUTIONS OF SULPHURIC, HYDROCHLORIC, AND PHOSPHORIC ACIDS

By N. S. BAYLISS* and D. W. WATTS*†

[Manuscript received February 15, 1956]

Summary

The ultraviolet spectrum of sodium nitrite in aqueous sulphuric acid is essentially that of nitrous acid below 40 per cent. acid, and that of nitrosonium ion above 70 per cent. acid. In the intermediate range there is evidence that the nitroacidium ion (H_2NO_2^+) is an important constituent of the solution. Equilibria involving the three species have been calculated using activity data for water and sulphuric acid. Similar results are obtained in aqueous phosphoric acid as a solvent. In hydrochloric acid of low water activity the high chloride activity causes what appears to be almost total conversion to nitrosyl chloride.

The ultraviolet spectrum of the nitrosonium ion is a structureless transition with $\epsilon_{\text{max.}} = 3850$ at about 46 kK (2200 Å). The nitroacidium ion does not absorb appreciably within the accessible range.

I. INTRODUCTION

The present work began as a spectrophotometric study of the Gay-Lussac acid of a conventional chamber sulphuric acid plant. The early synthetic solutions were made by dissolving nitrosonium bisulphate (nitrosyl sulphuric acid) in sulphuric acid of suitable concentration; but it was soon found that sodium nitrite solutions gave identical spectra. Furthermore, the (to us) unexpected stability of the latter solutions induced us to study their spectra over a wide range of sulphuric acid concentration, in order to obtain additional evidence concerning the spectra and equilibria of species such as the nitrosonium and nitroacidium ions, NO^+ and H_2NO_2^+ , and also the nitrous acid molecule.

Previous investigations of similar systems have been incomplete. Schlesinger and Salathe (1923) used a relatively crude spectrophotometric method to study the hydrolysis of nitrosonium bisulphate to nitrous acid in aqueous sulphuric acid, and found that nitrous acid was not formed in sulphuric acid of 50 per cent. concentration or greater. Subsequently, Angus and Leckie (1935) obtained Raman evidence to show that in similar solutions the nitrosonium ion (NO^+) was present at high sulphuric acid concentration but appeared to be hydrolysed completely if the sulphuric acid was 55 per cent. or less. Schmid and Maschka (1941) and Maschka (1953a, 1953b) studied the hydrolysis of nitrosyl chloride

* Department of Chemistry, University of Western Australia, Nedlands, W.A.

† Cuming-Smith & Mount Lyell Farmers Fertilizers Ltd. Research Student 1955. This paper is based in part on a thesis submitted by Mr. D. W. Watts in January 1955 as part of the requirements for the honours degree of B.Sc. in the University of Western Australia.

in hydrochloric acid using a photometric method, and of nitrosonium bisulphate in sulphuric acid using a kinetic method. They interpreted their results on the assumption that besides nitrous acid the only other nitrogen-containing species were nitrosyl chloride and nitrosonium bisulphate respectively. Deschamps (1953), in a preliminary study, found the edge of the intense ultraviolet absorption of the nitrosonium ion in solutions containing nitrosonium bisulphate; but his solutions were probably too concentrated to enable him to observe the maximum. While a preliminary account of the present work (Bayliss and Watts 1955) was in the press, Addison and Lewis (1955), in a comprehensive review of the properties of the nitrosyl group, referred to their own unpublished work showing that the ultraviolet spectrum of the nitrosonium ion occurs in 80–90 per cent. sulphuric acid.

In the present paper it will be seen that our results concerning the spectra and stability ranges of nitrosonium ion and nitrous acid in acid solutions are in qualitative agreement with the earlier work, but that to account for the properties of the solutions in the intermediate acid range it is necessary in addition to postulate the presence of a third species (nitroacidium ion) at a relatively substantial concentration.

II. EXPERIMENTAL

The solutions, whose absorption spectra were measured, consisted of sodium nitrite dissolved in aqueous sulphuric, hydrochloric, and orthophosphoric acids of various concentrations. Preliminary experiments included solutions of nitrosyl sulphuric acid (nitrosonium bisulphate) in sulphuric acid; but after it was established that these were identical spectrophotometrically with sodium nitrite solutions, the latter solute was used exclusively.

The sodium nitrite, sulphuric acid, and hydrochloric acid were of analytical reagent grade and were used without further purification. Orthophosphoric acid was purified and concentrated by the method of Archibald (1932) and the nitrosyl sulphuric acid used in the preliminary work was prepared according to Booth (1939).

The concentrations of the sulphuric and orthophosphoric acids used as solvents were determined by measuring their densities. Concentrations of hydrochloric acid solvents were determined by the precipitation of silver chloride and by conductance measurements (Owen and Sweeton 1941). The absorption spectrum of nitrous acid was studied conveniently in solutions of about $M/30$ with respect to sodium nitrite. These were made up by cooling the solvent to -10°C and adding it to a weighed amount of sodium nitrite. The cooling was found to prevent decomposition and the need for a subsequent determination of the nitrite content of the solutions. The study of the nitrosonium ion absorption required solutions of the order of $M/3000$, which were prepared from the above by volume dilution.

The absorption spectra were measured in 1 cm silica cells in a Beckman spectrophotometer (model DU) equipped with a photomultiplier detector. The maximum nominal bandwidth was 10 \AA except near the ultraviolet cut-off of the orthophosphoric acid solutions, where it was increased to 40 \AA .

III. RESULTS AND DISCUSSION

The optical density D of a solution is defined by $D = \log_{10} I_0/I$, where I_0 and I are the incident and transmitted intensities respectively. Using M to denote the total nitrite concentration in mole l^{-1} , the results have been calculated in terms of D/M as a function of the frequency in kaysers (K). For a cell of length 1 cm, D/M becomes the molar extinction coefficient ϵ in the case when the dissolved nitrite is present as a single molecular species. Thus it can be seen that the fraction of the nitrite in this form under any other solvent condition is given by $D/M\epsilon$.

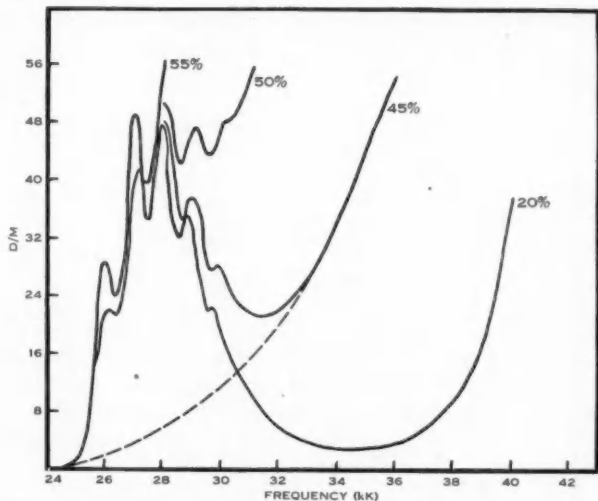


Fig. 1.—Absorption spectra of sodium nitrite in sulphuric acid of concentrations varying from 20 to 55 per cent. by weight. The banded absorption is that of nitrous acid. The broken line shows the method of subtracting the nitrosonium background in order to obtain nitrous acid concentrations.

(a) Sulphuric Acid as Solvent

The spectra may be discussed conveniently in relation to the following three concentration ranges of the sulphuric acid solvent:

(i) In the low range below 30 per cent. by weight of sulphuric acid the spectrum as shown in Figure 1 is that of the nitrous acid molecule (Landolt-Börnstein 1950), and consists of a weak transition near 27 kK showing well-marked vibrational structure.

(ii) In the high range above 50 per cent. sulphuric acid, the nitrous acid spectrum is replaced by a much more intense transition (Fig. 2) which is structureless with a broad maximum lying between 38 and 46 kK according to the sulphuric acid concentration.

(iii) In the intermediate range between 30 and 55 per cent. sulphuric acid the absorption curves (Fig. 1) show the nitrosonium ion and the nitrous acid spectra superimposed, the weak banded absorption of the latter species appearing on the low frequency toe of the much more intense transition of the nitrosonium ion.

We have used these spectra to calculate the proportions of the total nitrite present as nitrous acid and as nitrosonium ion throughout the sulphuric acid concentration range, using the following assumptions.

(1) In 95 per cent. sulphuric acid the dissolved nitrite is taken to be present entirely as nitrosonium ion. This is in accordance with the fact that the function D/M at the peak has reached a practically constant maximum value at this

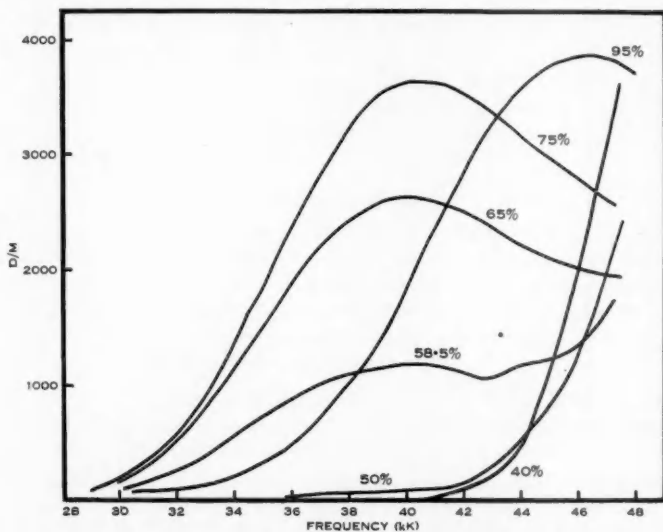


Fig. 2.—The absorption spectrum of sodium nitrite in sulphuric acid of concentrations ranging from 40 to 95 per cent. by weight. The intense broad band is that of the nitrosonium ion.

concentration, and also with the evidence from Raman spectra (Angus and Leckie 1935; Millen 1950). The value of D/M at this concentration is thus the true molar extinction coefficient of the nitrosonium ion (Table 1).

(2) In 30 per cent. sulphuric acid (and below) the dissolved nitrite is assumed to occur entirely as nitrous acid, D/M giving the molar extinction coefficients (Table 2).

(3) Where the nitrous acid and the nitrosonium ion spectra are superimposed, their contributions have been separated by extrapolating the nitrosonium ion spectrum to lower frequencies (see broken curve in Fig. 1) in such a way that the derived nitrous acid absorption curves maintained constant intensity ratios between the vibrational bands.

The results of the calculations are given in Table 3, where it is seen that in the range between 35 and 75 per cent. sulphuric acid the combined contributions from the nitrous acid and nitrosonium ion do not account for the total nitrite content of the solutions. We are thus led to the conclusion that some other species must be present in this acid range, and furthermore that it is a

TABLE 1
THE ABSORPTION OF NITROSONIUM ION

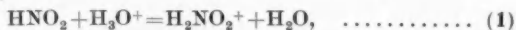
H ₂ SO ₄ Conc. (wt. %)	D/M	Position of Maximum (kK)
95.0	3850	46.3
85.0	3810	42.0
80.0	3800	41.0
75.0	3630	40.4
70.0	3240	40.0
65.0	2650	39.8
60.0	1550	39.4
58.5	1150	39.2
57.0	600	38.9
55.0	310	38.5
50.0	50	—

species that apparently does not contribute, except for slight changes in background, to the absorption spectrum in the frequency range we have investigated. Bearing in mind that proton transfer and dehydration respectively are dominant reactions in moderate and high sulphuric acid concentrations, we suggest that this intermediate form is the *nitroacidium* ion H₂NO₂⁺ (Ingold 1953; Anbar

TABLE 2
EXTINCTION COEFFICIENTS FOR NITROUS ACID BANDS CORRECTED FOR BACKGROUND

Band	Frequency (kK)	$\epsilon_{\max.}$		
		In H ₂ SO ₄	In HCl	In H ₃ PO ₄
1	26.0	28.6	28.9	28.8
2	27.0	48.5	49.6	49.2
3	28.0	45.1	46.0	46.8
4	28.8	34.5	33.2	34.5
5	29.7	20.7	20.7	21.1

and Taube 1954; Bunton, Llewellyn, and Stedman 1955) formed in the following sequence of equilibria:



to which we assign the equilibrium constants K_1 and K_2 respectively. Table 3 gives the nitroacidium ion fraction derived by difference, and the relative

concentrations of the three species, plotted against sulphuric acid concentration, are shown in Figure 3.

The validity of the equilibria of the preceding paragraph can be checked from the experimental data, subject to some reservations. Denoting activity and concentration (mole l⁻¹) by parentheses and square brackets respectively, equation (2) gives

$$\frac{(\text{NO}^+)}{(\text{H}_2\text{NO}_2^+)} = \frac{K_2}{(\text{H}_2\text{O})} \quad \dots\dots\dots (3)$$

TABLE 3
RESULTS IN SULPHURIC ACID

H ₂ SO ₄ (wt. %)	<i>m</i>	(H ₂ SO ₄) at 25 °C*	(H ₂ O) at 25 °C†	Fraction of Total Nitrite as:		
				HNO ₂	NO ⁺	H ₂ NO ₂ ⁺
40.0	6.79	34.5	0.56	0.99	—	0.01
42.5	7.53	73.2	0.505	0.97	—	0.03
45.0	8.34	160	0.460	0.93	—	0.07
47.5	9.22	357	0.405	0.83	—	0.17
50.0	10.2	817	0.350	0.72	0.01	0.27
52.5	11.3	1830	0.300	0.54	0.04	0.42
55.0	12.4	4270	0.250	0.37	0.08	0.55
57.5	13.8		0.205	0.26	0.18	0.56
60.0	15.3		0.160	0.195	0.41	0.395
62.5	17.0		0.138	0.145	0.58	0.275
65.0	18.9		0.093	0.105	0.69	0.205
67.5	21.2		0.067	0.07	0.77	0.16
70.0	23.8		0.046	0.04	0.84	0.12
72.5	26.9		0.029	0.015	0.89	0.095
75.0	30.6		0.0173	0.005	0.94	0.055
77.5				—	0.97	0.03
80.0	40.8		0.0052	—	0.985	0.015
82.5				—	0.99	0.01
85.0	57.7		0.0016	—	0.995	0.005
87.5				—	1.00	—
90.0	91.7			—	1.00	—

* Harned and Hamer (1935).

† Jones (1951).

Since the nitroacidium and nitrosonium ions are positive ions of equal charge at low concentration in the same medium, it is reasonable to assume that their activity coefficients are equal, giving the following in terms of concentrations:

$$\frac{[\text{NO}^+]}{[\text{H}_2\text{NO}_2^+]} = \frac{K_2}{(\text{H}_2\text{O})} \quad \dots\dots\dots (4)$$

an equation which can be checked against our experimental concentration ratio, using in addition the data of Jones (1951) for the activity of water in aqueous sulphuric acid. Figure 4 shows that the plot of [NO⁺]/[H₂NO₂⁺] against 1/(H₂O) is reasonably linear within the range 60–80 per cent. sulphuric

acid, where (H_2O) varies by a factor of 30. We found the linear relation to fail below 60 per cent. sulphuric acid; but in this region the spectrophotometric determination of $[NO^+]$ is rather inaccurate.

The $[H_2NO_2^+]/[HNO_2]$ ratio of equation (1) is more difficult to check. From (1) we derive

$$\frac{(H_2NO_2^+)}{(HNO_2)} = \frac{K_1(H_3O^+)}{(H_2O)}, \dots\dots\dots (5)$$

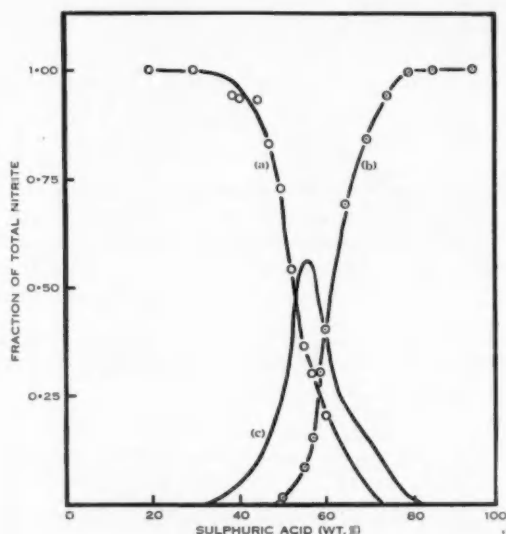


Fig. 3.—Distribution of total nitrite between the three forms: (a) nitrous acid, (b) nitrosonium ion, and (c) nitroacidium ion; plotted as a function of sulphuric acid concentration.

a relation whose consideration involves the problem of single ion activities, particularly that of H_3O^+ . After many trials, we found empirically that the experimental results closely obeyed the following relation (see Fig. 5):

$$\frac{[H_2NO_2^+]}{[HNO_2]} = \text{constant } (H_2SO_4), \dots\dots\dots (6)$$

within the range 40 to 50 per cent. sulphuric acid, where the sulphuric acid activity (Harned and Hamer 1935) varies by a factor of 50.

Now the activity data for sulphuric acid depend on the consideration of the equilibria



The formal treatment of these equilibria, even though (8) is that of a rather weak acid, involves the convention (i.e. assignment of standard states) that each has unit equilibrium constant (Lewis and Randall 1923). If m is the molal

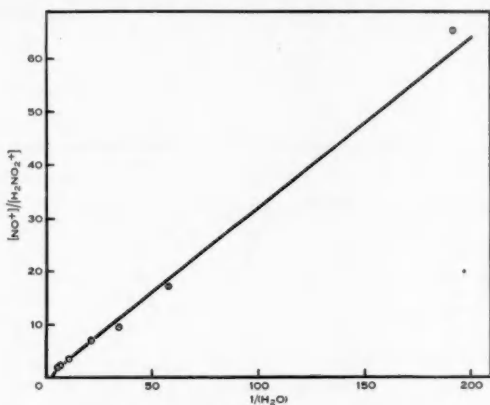


Fig. 4.—Curve showing validity of equation (4).

concentration of sulphuric acid, and γ , γ_+ , γ_- , and γ_{--} the molal activity coefficients respectively of the H_2SO_4 molecule, H^+ , HSO_4^- , and SO_4^{--} , then the following relation holds:

$$m\gamma = m^2\gamma_+\gamma_- = 4m^3\gamma_+^2\gamma_{--} \quad \dots\dots\dots (9)$$

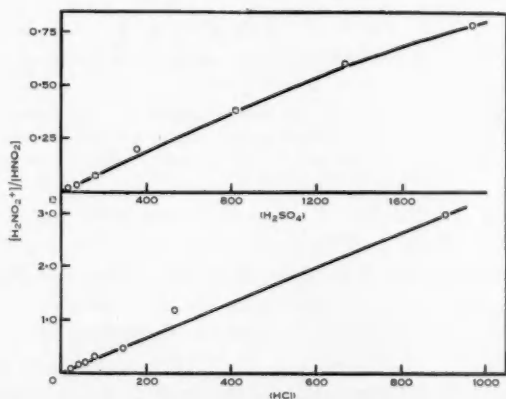


Fig. 5.—Curves showing validity of equation (6) (upper curve) and equation (17) (lower curve).

Although the properties of sulphuric acid in our experimental range can be represented almost entirely in accordance with equation (7) (Robinson and Stokes 1955), the extrapolation to infinite dilution needed to obtain activity

coefficients involves the consideration of (8) as well, and in fact the data of Harned and Hamer (1935), from which we calculated $(\text{H}_2\text{SO}_4)_\pm$, are expressed in terms of the mean activity coefficient γ_\pm such that

$$\gamma_\pm = (\gamma_+^2 \gamma_-)^{1/3}, \dots\dots\dots (10)$$

and

$$(\text{H}_2\text{SO}_4) = 4m^3 \gamma_\pm^3. \dots\dots\dots (11)$$

Since the thermodynamic data relating to sulphuric acid are expressed in terms of the imaginary species H^+ , we rewrite equation (1) in the form



with equilibrium constant K'_1 , giving

$$\frac{(\text{H}_2\text{NO}_2^+)}{(\text{HNO}_2)} = K'_1(\text{H}^+). \dots\dots\dots (13)$$

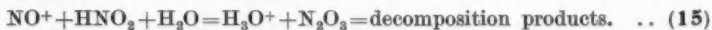
We now assume that all neutral species, such as HNO_2 and H_2SO_4 to the extent that they are present, have the same activity coefficient γ , and that all singly charged positive ions have the same activity coefficient γ_+ . Furthermore, since HNO_2 and H_2NO_2^+ are at very low concentration, the activity and molality of H^+ are that of the solvent, giving*

$$\begin{aligned} \frac{[\text{H}_2\text{NO}_2^+]}{[\text{HNO}_2]} &= K'_1(m\gamma_+)(\gamma/\gamma_+) = K'_1(m\gamma) \\ &= K'_1(\text{H}_2\text{SO}_4). \dots\dots\dots (14) \end{aligned}$$

Equation (14) is identical with the empirical relation of Figure 5.

Two interesting properties of the sulphuric acid system were observed qualitatively.

Solutions of sodium nitrite in sulphuric acid were found to be unexpectedly stable except in the range 55–60 per cent. sulphuric acid, where observable decomposition occurred during the time required to measure a spectrum (30 min). We have suggested (Bayliss and Watts 1955) that the instability is associated with the mutual presence in this range of nitrous acid molecules and nitrosonium ions leading to a reaction such as



Our experimental work gave no spectrophotometric evidence for the presence of N_2O_3 , and we have therefore omitted reactions such as (15) from consideration in connexion with the equilibria (1), (2), and (12). This result is not inconsistent with the existence of N_2O_3 as an important kinetic intermediate in the decomposition process.

The rate of solution of solid sodium nitrite is definitely lowered in sulphuric acid of over 70 per cent. concentration. Since this is the range where the nitrite

* This equation contains two different concentration units, namely the molality m of sulphuric acid and the molarities $[\text{H}_2\text{NO}_2^+]$ and $[\text{HNO}_2]$ as determined spectrophotometrically. This mixture is allowable since it involves only the ratio of the molarities.

enters the solution almost entirely as nitrosonium ion, the phenomenon is possibly the result of the fact that the dehydration of the nitroacidium ion is a slow reaction.

(b) *Hydrochloric Acid as Solvent*

If the equilibria (1) and (2) are correct, they should be observable in other acids as solvent. We have accordingly measured the spectra of sodium nitrite dissolved in hydrochloric acid and in orthophosphoric acid over a wide range of acid concentrations.

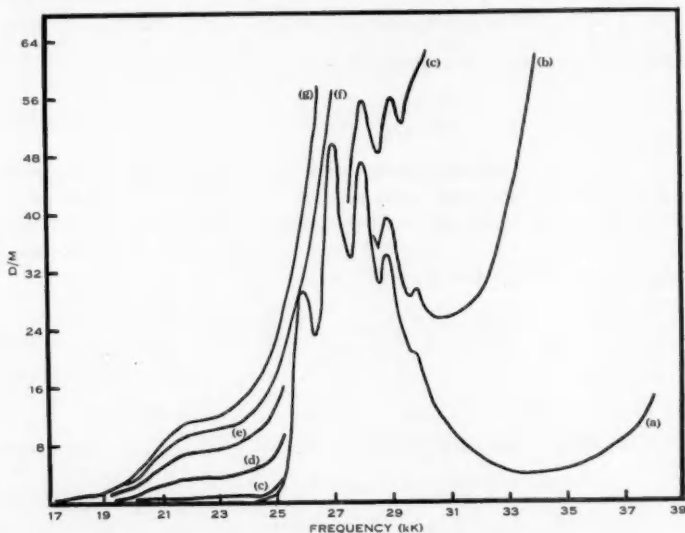


Fig. 6.—Absorption spectra of sodium nitrite dissolved in hydrochloric acid of concentrations: (a) 1.5M; (b) 3.5M; (c) 4.5M; (d) 5.0M; (e) 6.0M; (f) 8.0M; (g) 10M. The banded absorption between 25 and 31 kK is due to nitric acid; the transition between 19 and 25 kK is ascribed to nitrosyl chloride.

Figure 6 shows typical spectra in hydrochloric acid, including the banded absorption of nitrous acid and at lower frequency (near 22 kK) a transition which first becomes apparent in about 4M hydrochloric acid and increases thereafter in intensity as the acid concentration approaches our limiting value of 11M. This transition is due to the nitrosyl chloride molecule. The increased intensity at higher frequency is doubtless due to the nitrosonium ion, but owing to the instability of the required dilute solutions of sodium nitrite we were unable to follow accurately this transition to its maximum. However, it was possible to separate the nitrous acid absorption from the background absorptions of nitrosyl chloride and nitrosonium ion and thus to get values of $[\text{HNO}_2]$, the fraction of the total nitrite present as nitrous acid (Table 4). The extinction coefficients thus obtained are given in Table 2.

It thus seems clear that in hydrochloric acid one must consider equilibria (1) and (2) together with



Unfortunately, this cannot be checked as completely as in the sulphuric acid case since the experimental data do not enable us to determine either $[\text{NO}^+]$ or $[\text{NOCl}]$ in the high acid range. As mentioned, we could not measure the maximum due to nitrosonium ion, and also since the function D/M in the nitrosyl chloride region did not reach a maximum even in the most concentrated acid (Table 5), we could not establish the extinction of pure nitrosyl chloride. In the more dilute acid range ($<5\text{M HCl}$) we can obtain $[\text{H}_2\text{NO}_2^+]$ and $[\text{HNO}_2]$,

TABLE 4
RESULTS IN HYDROCHLORIC ACID

HCl Conc. (mole l ⁻¹)	<i>m</i>	(HCl) at 25 °C*	Fraction of Total Nitrite as HNO_2
1.51	1.58	1.96	1.00
2.02	2.13	4.41	1.00
2.52	2.68	9.61	1.00
3.03	3.24	20.2	0.94
3.53	3.81	39.7	0.87
3.79	4.12	56.3	0.84
4.04	4.42	77.4	0.77
4.54	5.02	144	0.69
5.03	5.64	266	0.46
6.03	6.90	900	0.25
8.04	9.67	—	<0.03

* Robinson and Stokes (1949).

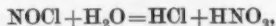
the fractions of the total nitrite present as nitroacidium ion and nitrous acid molecules, from the absorption curves if it is assumed that $[\text{NOCl}]$ and $[\text{NO}^+]$ are negligible. That this is true for nitrosyl chloride is apparent from the absorption curves (Fig. 6).

Furthermore the dehydration of the nitroacidium ion to give nitrosonium ions is governed by the water activity (eqn. (2)), and even in 6M hydrochloric acid the water activity is about the same as in 45 per cent. sulphuric acid, where the dehydration reaction (2) is negligible (Fig. 3). On this basis the relation

$$\frac{[\text{H}_2\text{NO}_2^+]}{[\text{HNO}_2]} = \text{constant (HCl)}, \quad \dots\dots\dots (17)$$

was found to hold over the range 2.0 to 6.0M hydrochloric acid, where the activity (HCl) varies 45-fold (see Fig. 5). Equation (17) is analogous to (6) and may be derived similarly.

Schmid and Maschka (1941) have calculated an equilibrium constant for the reaction



using spectrophotometrically determined values for the nitrosyl chloride concentration. It seems to the authors that their results are invalid because they have assumed the existence of only the two nitrogen species, nitrosyl

TABLE 5
ABSORPTION OF NITROSYL CHLORIDE IN HYDROCHLORIC ACID

HCl Conc. (mole l ⁻¹)	<i>D/M</i> at 23,260 K	<i>D/M</i> at 21,750 K
4.04	1.80	0.50
4.54	2.63	1.75
5.03	3.68	3.05
6.03	7.61	6.65
7.10	9.9	8.7
8.00	10.4	9.0
8.20	10.3	9.0
8.70	10.8	9.4
9.20	10.8	9.5
9.7	11.6	10.0
10.0	12.4	10.6
10.2	12.9	10.9
11.4*	13.9*	11.8*

* Results for *D/M* could be 5 per cent. low due to solution and solvent instability.

chloride and nitrous acid, and because their spectrophotometric measurements were made at a frequency of about 23.3 kK ($\sim 4300 \text{ \AA}$) which is not at the maximum of the visible nitrosyl chloride transition (Fig. 6). Furthermore,

TABLE 6
RESULTS IN PHOSPHORIC ACID

Phosphoric Acid Concentration (wt. %)	Fraction of Total Nitrite as :		
	HNO ₂	NO ⁺	H ₂ NO ₂ ⁺
30	1.00	—	—
40	0.99	—	0.01
50	0.98	—	0.02
55	0.97	—	0.03
60	0.96	0.01	0.03
65	0.92	0.02	0.06
70	0.84	0.05	0.11
75	0.69	0.09	0.22
80	0.47	0.21	0.32
85	0.20	0.64	0.16
90	0.02	0.95	0.03
95	—	0.995	0.005
100	—	1.00	—

contrary to Schmid and Maschka, the present results (Table 5) suggest that even at this frequency the function *D/M* has not reached a maximum in the most concentrated acid and thus it seems that one cannot assume all the nitrite is in the form of nitrosyl chloride in 11M hydrochloric acid.

(c) *Orthophosphoric Acid as Solvent*

The spectrophotometric results for this solvent are identical with those found in sulphuric acid, except the actual maximum of the nitrosonium ion transition is not reached because it is beyond the solvent cut-off.

However, using values of the function D/M at 38 kK it was possible, assuming all the nitrite in 99 per cent. phosphoric acid to be in the form of nitrosonium ion, to obtain a value for the extinction of the species at this frequency (ϵ_{NO^+} , 38.0 kK = 2160).

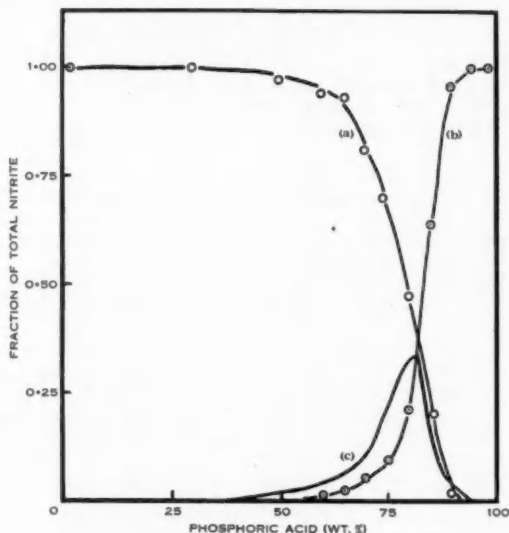


Fig. 7.—Distribution of total nitrite amongst the three forms : (a) nitrous acid, (b) nitrosonium ion, and (c) nitroacidium ion ; plotted as a function of phosphoric acid concentration.

This method necessarily introduces the assumption that there is no shift in the position of the nitrosonium ion absorption with changes in solvent concentration. This assumption cannot, of course, be tested, but the form of the absorption curves suggests that the error introduced is not large.

The results for this system are presented in Tables 2 and 6 and in Figure 7. A comparison of Figure 7 with Figure 3 shows that the equilibria in the sulphuric acid and in the phosphoric acid systems are qualitatively similar. The nitrous acid range is greater and the nitrosonium ion range smaller in the latter system as compared with the former. This is consistent with the lower hydrogen ion activity in phosphoric acid. That the nitroacidium ion exists over a smaller range in phosphoric acid is undoubtedly due to the fact that in hydrogen ion activities great enough to form this ion the water activity is low and thus the nitrosonium ion becomes the stable species.

A quantitative treatment of this system, similar to that given in the case of sulphuric acid, could not be made because activity data are not available.

IV. ACKNOWLEDGMENTS

The investigation of the sulphuric acid system was suggested initially by Cumming Smith and Mt. Lyell Farmers Fertilizers Ltd., who have given support in the form of a studentship to one of us (D.W.W.), as well as in the purchase of apparatus and chemicals. We are also indebted to the Research Fund of the University of Western Australia for some financial support.

V. REFERENCES

- ADDISON, C. C., and LEWIS, J. (1955).—*Quart. Rev.* **9**: 115.
ANBAR, M., and TAUBE, H. (1954).—*J. Amer. Chem. Soc.* **76**: 6243.
ANGUS, W. R., and LECKIE, A. H. (1935).—*Proc. Roy. Soc. A* **149**: 327.
ARCHIBALD, E. H. (1932).—"Preparation of Pure Inorganic Substances." (John Wiley & Sons Inc.: New York.)
BAYLISS, N. S., and WATTS, D. W. (1955).—*Chem. & Ind.* **1955**: 1353.
BOOTH, H. S. (1939).—"Inorganic Syntheses." Vol. 1. (McGraw-Hill Book Co. Inc.: New York and London.)
BUNTON, C. A., LLEWELLYN, D. R., and STEDMAN, G. (1955).—*Nature* **175**: 83.
DESCHAMPS, J. (1953).—*Mémor. Serv. Chim. Etat* **38**: 335.
HARNED, H. S., and HAMER, W. J. (1935).—*J. Amer. Chem. Soc.* **57**: 27.
INGOLD, C. K. (1953).—"Structure and Mechanism in Organic Chemistry." pp. 398-400. (G. Bell & Sons Ltd.: London.)
JONES, F. R. (1951).—*J. Appl. Chem.* **1**: 144.
LANDOLT-BÖRNSTEIN (1950).—"Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik." (Springer-Verlag: Berlin, Göttingen, Heidelberg.)
LEWIS, G. N., and RANDALL, M. (1923).—"Thermodynamics and the Free Energy of Chemical Substances." (McGraw-Hill Book Co. Inc.: New York and London.)
MASCHKA, A. (1953a).—*Mh. Chem.* **84**: 855.
MASCHKA, A. (1953b).—*Mh. Chem.* **84**: 872.
MILLEN, D. J. (1950).—*J. Chem. Soc.* **1950**: 2589.
OWEN, B. B., and SWEETON, F. H. (1941).—*J. Amer. Chem. Soc.* **63**: 2811.
ROBINSON, R. A., and STOKES, R. H. (1949).—*Trans. Faraday Soc.* **45**: 612.
ROBINSON, R. A., and STOKES, R. H. (1955).—"Electrolyte Solutions." (Butterworth Scientific Publications: London.)
SCHLESINGER, H. I., and SALATHE, A. (1923).—*J. Amer. Chem. Soc.* **45**: 1863.
SCHMID, H., and MASCHKA, A. (1941).—*Z. physik. Chem.* **49**: 171.

NOTE ADDED IN PROOF

Since the present paper was submitted we have seen an important review on the properties of nitrosonium ion (Seel, F. (1956).—*Angew. Chem.* **68**: 272).

Professor Abel (personal communication) has also drawn our attention to his work on the nitrosonium ion, particularly as it concerns reactions in the lead chamber process (Abel, E., Schmid, H., and Pollak, F. (1936).—*Mh. Chem.* **69**: 125; Abel, E. (1949).—*Mh. Chem.* **80**: 379).

THE SURFACE CONDUCTANCE OF KAOLINITE

By N. STREET*

[Manuscript received March 5, 1956]

Summary

The surface conductance of kaolinite particles has been determined and compared with values calculated from measured ζ -potentials. A reasonable measure of agreement between these values suggests that the theory is adequate, and indicates that further information about the behaviour of kaolinite suspensions might be gained from careful measurements of this phenomenon. The information can also be used to determine the axial ratios of clay particles.

I. INTRODUCTION

The existence of an electric double layer at the solid-solution interface of the clay-water system means that a higher concentration of ions exists near to the phase boundary than in the bulk solution. As a consequence, electrokinetic phenomena such as electro-osmosis etc. are recognized; also, there is a surface conductance, which may be positive, negative, or zero, dependent on the charge on the surface and the mobilities of the ions concerned (Cole 1933). Since the double layer contains more ions than the bulk of the liquid, then there will be a tendency for a higher conductance to exist in proximity to the surface (charge effect), but since these ions concentrated at the surface may well be of lower mobility than the average in the bulk of the solution, thus the balance between number and type (mobility effect) of the double layer ions may give the effects noted by Cole. There is also an electro-osmotic effect (in D.C. and low frequency A.C. fields) since there are not equal numbers of oppositely charged ions in the double layer. Now the magnitude of the surface conductance is of importance in regard to the interpretation of electrophoresis measurements, and the calculation of ζ -potentials from them, which are in turn important in such fields as the interpretation of electric well log data, adsorption phenomena, and colloid stability.

The interpretation of measurements of ζ -potential carried out by electrophoresis is affected by the magnitude of the surface conductance (Booth 1948; Henry 1948) such that the value calculated by Henry's (1931) equation must be multiplied by

$$1 + \frac{\lambda_s}{K_1 a}, \dots\dots\dots (1)$$

where λ_s =surface conductivity (ohm^{-1}),
 K_1 =filtrate conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$),
 a =radius of particle (cm),

* Department of Geology, University of Melbourne.

in order to give the true value corrected for surface conductance. From a study of the equation for the calculation of surface conductance from ζ -potential (see below) it can be seen that a knowledge of ζ and a is sufficient to enable the surface conductance to be calculated. It is a fact that the correction will not be great unless a is very small, and ζ is very large, *if the surface conductance has a normal value*, that is, that calculated from the true ζ -potential. In this case, the surface conductance correction is provided for in the relaxation correction (Overbeek 1943). If, however, the surface conductance is for some reason much greater than normal then the "Henry" ζ must be corrected by a not inconsiderable factor. The majority of investigations reported have been conducted on glass surfaces, and, in the majority of cases, have given values much greater than the theoretical, so that Overbeek (Kruyt 1952) has suggested that conductance may occur through a swollen surface layer, that is, be independent of the electrokinetic phenomena.

II. THEORY

The theory of surface conductance has been worked out by several authors, for example, Bikerman (1935) and Urban, White, and Strassner (1935), the expression obtained for univalent ions is as follows:

$$\lambda_s = \sqrt{\left(\frac{DRT}{2\pi F^2}\right)} \left[(e^{\zeta/2kT} - 1) \left(L_+ + \frac{DRT}{2\pi\eta} \right) + (e^{-\zeta/2kT} - 1) \left(L_- + \frac{DRT}{2\pi\eta} \right) \right], \quad \dots \dots \dots (2)$$

where λ_s = surface conductivity (ohm^{-1}),

D = dielectric constant,

R = gas constant (8.324×10^7 ergs mole $^{-1}$ deg $^{-1}$),

T = absolute temperature,

C = concentration (mol cm $^{-3}$),

F = Faraday (96,500 C),

ζ = ζ -potential,

k = Boltzmann's constant,

L_+ , L_- = mobility of cation and anion respectively,

e = electronic charge,

η = viscosity (P).

The expression $DRT/2\pi\eta$ gives the electro-osmotic contribution to the surface conductance.

Urban, White, and Strassner (1935) evolved an equation to add a contribution to the surface conductance caused by the mobility of the ions in the Stern layer. However, it would seem most unlikely that the Stern layer ions would have sufficient mobility to contribute greatly to the surface conductance.

III. MEASUREMENT OF SURFACE CONDUCTANCE

In the case of a porous plug packing, the method of measurement is simply to determine the bulk conductance of the solution being used, then the conductance of the solution whilst in the interstitial pores of the plug. This latter is achieved (O'Connor, Street, and Buchanan 1954) with the aid of a cell

constant determined by using an electrolyte of such concentration that the surface conductance is negligible (Bikerman 1933, 1935, 1940).*

Then

$$\lambda_s = \Delta\lambda \cdot \frac{A}{S}, \quad \dots \dots \dots (3)$$

where $\Delta\lambda$ is the excess of conductance exhibited by the solution when present in the pores of the plug, A is the cross-sectional area of the plug, S is the perimeter of cross section, and λ_s is the surface conductance. O'Connor, Street, and Buchanan (1954) show that the factor A/S can be determined from flow and electrical data.

$$A/S = 0.00184(C\eta Q)^{1/2},$$

where C = cell constant of the plug,

η = viscosity of the flowing liquid (P),

Q = rate of flow ($\text{cm}^3 \text{ min}^{-1} \text{ cm}^{-1}$ mercury).

However, the comparison of electrokinetic and surface conductance data is difficult using a plug, since if the plug is packed with material coarse enough to give reliable ζ -potential data, then the surface area is so small as to render the surface conductance measurements dubious.

The problem of calculating the surface conductance from measurements on a suspension was undertaken by Fricke and Curtis (1936), who showed that

$$\lambda_s = \frac{(K/K_1 - 1) + \frac{1}{2}\rho(K/K_1 + 2)}{\rho(K/K_1 + 2) - (K/K_1 - 1)} K_1 a, \quad \dots \dots \dots (4)$$

where K = specific conductivity of the suspension ($\text{ohm}^{-1} \text{ cm}^{-1}$),

K_1 = specific conductivity of the suspending medium ($\text{ohm}^{-1} \text{ cm}^{-1}$),

ρ = volume concentration of solid in suspension,

a = radius of particles in suspension.

The results obtained in this work were at first calculated using this formula. However, although consistent results were obtained by Fricke and Curtis using concentrated suspensions, it was not found possible to obtain consistent results between measurements at different low volume concentrations. It was not, of course, feasible in this study to use high volume concentrations, since the viscosities, particularly of the flocculated suspensions soon become too great.

If instead of using the Fricke and Curtis equation the problem is approached in the same manner as it is for a porous plug, then it can be seen that a factor F must exist such that when the conductivity of the suspension is multiplied by it, then the conductivity of the liquid in the pores is obtained. In the case of a plug, this F (the "formation factor" of Wyllie and Gregory 1953) is determined from a measurement of the cell constant of the plug by using a solution of sufficiently high concentration for the surface conductance to be negligible. However, the use of highly concentrated electrolyte solutions is inconvenient

* The results of Winsauer and McCardell (1953) suggest that for the surface conductances to be negligible the cell constant should be measured with electrolyte of the order of 1N.

with clay suspensions, and further, the results of Winsauer and McCardell (1953) indicate that the surface conductance effect is still persistent at very high electrolyte concentrations.

The Maxwell (1904) equation for a suspension of spheres,

$$\frac{K/K_1 - 1}{K/K_2 + 2} = (1 - \varphi) \frac{K_2/K_1 - 1}{K_2/K_1 + 2}, \quad \dots \dots \dots (5)$$

where K_2 is the specific conductivity of the spheres and φ the fractional fluid content, reduces to

$$\frac{K_1}{K} = \frac{3 - \varphi}{2\varphi}, \quad \dots \dots \dots (6)$$

when $K_2 = 0$. In the absence of surface conductance $FK - K_1 = 0$, that is, $F = K_1/K$, and hence

$$F_0 = \frac{3 - \varphi}{2\varphi}, \quad \dots \dots \dots (7)$$

where F_0 is the particular value of F for a dilute suspension of spherical particles. If surface conductance exists, then that surface conductance is equal to $FK - K_1$. This will be an excess of surface conductance applicable only to the particular concentration of particles being measured; if this surface conductance is multiplied by the volume of liquid contained in 1 c.c. of the suspension, and divided by the surface area of solid in 1 c.c. of the suspension, then the true specific surface conductance is obtained

$$\lambda_s = (FK - K_1) \frac{\varphi}{S_w}, \quad \dots \dots \dots (8)$$

when S_w = surface area of solid/c.c. of suspension.

For some purposes the ratio λ_s/a is sufficient, and, since

$$S_w = 4\pi a^2 N, \text{ and } \rho = \frac{4}{3}\pi a^3 N,$$

where N = number of particles/c.c., thus

$$S_w = 3\rho/a,$$

and

$$\frac{\lambda_s}{a} = (FK - K_1) \frac{\varphi}{3\rho}.$$

The choice of F may sometimes be difficult although the agreement found by Fricke and Curtis (using dilute suspension of spheres), between values of ρ calculated from specific gravity data and calculated from conductivity data by the Maxwell formula, lends support to F_0 being, in fact, a true value of the factor F under these conditions. Some other values that have been proposed for F are shown below.

Fricke (1924) : For Non-spherical Particles

$$F_1 = \frac{(x+1) - \varphi}{x\varphi}. \quad \dots \dots \dots (9)$$

Slawinski (1926): (i) For a Porous Plug

$$F_2 = \frac{(1.3219 - 0.3219\varphi)^2}{\varphi} \dots \dots \dots (10)$$

(ii) For a Suspension

$$F_3 = 1 + \frac{\rho}{p} \left[\frac{(1 + 0.3219p)^2}{1-p} - 1 \right], \dots \dots \dots (11)$$

where $p = x\rho^{2/3}$, and when

$$\begin{aligned} \rho < 0.15, \quad x &= 0.806, \\ 0.15 < \rho < 0.60, \quad x &= 0.806 + 0.1333\rho, \\ \rho > 0.60, \quad x &= 0.9047. \end{aligned}$$

Archie (1942)

$$F_4 = \varphi^{-1.3} \dots \dots \dots (12)$$

Winsauer et al. (1952)

$$F_5 = C\varphi^{-m} \dots \dots \dots (13)$$

The factor F_1 (Fricke 1924) is for use with non-spherical particles, and in the case of an oblate spheroid (to which these disk-shaped clay particles approximate), the term x is calculated as follows:

$$x = -\frac{1}{\beta + 1}, \dots \dots \dots (14)$$

where

$$\beta = \frac{1}{3} \left[\frac{2}{1 + (K_2/K_1 - 1)\frac{1}{2}M} + \frac{1}{1 + (K_2/K_1 - 1)(1 - M)} \right] \left[\frac{K_2}{K_1} - 1 \right], \dots (15)$$

where K_2 = conductivity of suspended medium, that is, ∞ for kaolinite, and K_1 = conductivity of suspending medium, and

$$M = \frac{J - \frac{1}{2} \sin 2J}{\sin^3 J} \cos J, \dots \dots \dots (16)$$

($\cos J = a/b$ for particles of axes a and b , $a < b$).

Using the axial ratio of 1:12 determined (Street 1956) for these kaolinite particles, and calculating according to the above equation, $x = 0.394$ and F_1 can be obtained for any φ from (9). Figure 1 shows a plot of F_0 , F_1 , F_3 , and F_4 over the range of ρ used in this work.

IV. EXPERIMENTAL

The experiments carried out on surface conductivity measurements were all conducted at 25 °C in a thermostat controlled to 0.01 °C. A normal Wheatstone bridge network was used, the oscillator providing A.C. of 1000 cycles. The procedure used was to determine the conductivity of a suspension of clay particles of known sp. gr. (and, therefore, known volume concentration), then after centrifuging to determine the conductivity of the filtrate after its equilibra-

tion to 25 °C in the thermostat. At first, attempts were made to construct a conductivity cell such that the centrifugation could be carried out in it; however, the centrifugal force required to sediment the deflocculated samples of clay was so great that the cell continually broke and this idea was abandoned.

A very pure kaolinite from Egerton, Victoria, was used; after fractionation and washing (including removal of organic matter by hydrogen peroxide treatment) it had a surface area, measured by the B.E.T. method (N_2 at liquid air temperature), of 176,000 cm^2/g . The preliminary measurements were conducted

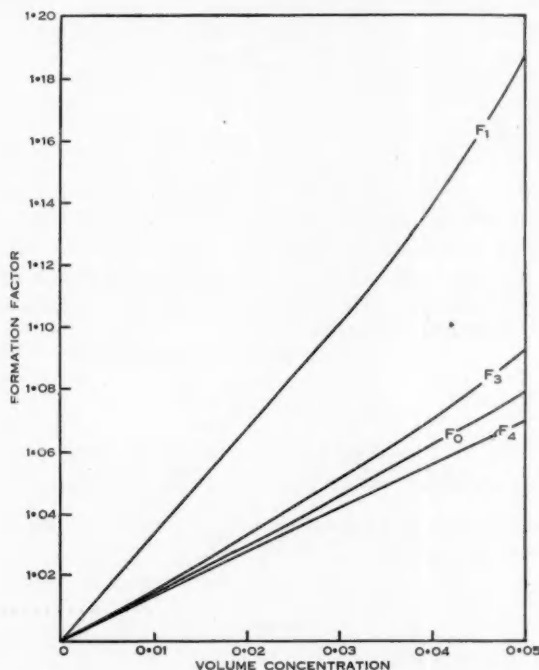


Fig. 1.—Factor "F" against volume concentration.

on clay leached with CaCl_2 and MgCl_2 solutions and washed free of electrolyte by continued centrifuging. The surface conductivity measurements were made throughout the washing period, and, for the CaCl_2 extra electrolyte was added to some samples to extend the range of measurements. In the case of the MgCl_2 the washing was continued to lower values of filtrate conductivity than for CaCl_2 . Measurements were also carried out on hydrogen clay during the washing period. Tables 1, 2, and 3 show the results for the Ca-kaolinite plus CaCl_2 , and Figures 2 and 3, respectively, the results for Mg-kaolinite plus MgCl_2 , and H-kaolinite. Table 4 presents the measured ζ -potentials of the H-kaolinite. In each case, the surface conductivity has been calculated assuming

TABLE 1

Ca-KAOLINITE PLUS CaCl_2 : FILTRATE-CONDUCTIVITY CONSTANT—SURFACE CONDUCTIVITY CALCULATED BY VARIOUS FACTORS

Volume Concentration, ρ	Filtrate Conductivity, K_1 ($\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-6}$)	Surface Conductivity ($\text{ohm}^{-1} \times 10^{-9}$) Calc. by Factor:*			
		F_0	F_1	F_3	F_4
0.0115	5.3	0.59	0.87	0.61	0.53
0.0217	5.3	0.60	0.85	0.65	0.58
0.0386	5.37	0.58	0.84	0.61	0.55
0.0493	5.34	0.59	0.86	0.62	0.56

* The columns headed F_0 , F_1 , F_3 , and F_4 are surface conductivity as calculated by these various F values.

TABLE 2

Ca-KAOLINITE PLUS CaCl_2 : SURFACE CONDUCTIVITY MEASURED AND CALCULATED

Volume Concentration, ρ	Filtrate Conductivity, K_1 ($\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-6}$)	Surface Conductivity ($\text{ohm}^{-1} \times 10^{-9}$)			
		Fricke and Curtis's (1936) Eqn. (4)	F_1	λ_z Calc.*	λ_z Calc.†
0.0113	2.88	0.50	0.64	0.25	0.38
0.0493	3.11	0.61	0.64	0.26	0.39
0.0287	3.19	0.54	0.71	0.27	0.41
0.0380	3.30	0.59	0.74	0.27	0.41
0.0446	3.62	0.70	0.80	0.28	0.42

* With ζ at 30 mV and no electro-osmose.

† With ζ at 30 mV and electro-osmose.

TABLE 3

Ca-KAOLINITE PLUS CaCl_2 : SURFACE CONDUCTIVITY MEASURED AND CALCULATED

Volume Concentration, ρ	Filtrate Conductivity, K_1 ($\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-6}$)	Surface Conductivity ($\text{ohm}^{-1} \times 10^{-9}$)			
		Fricke and Curtis's (1936) Eqn. (4)	F_1	λ_z Calc.*	λ_z Calc.†
0.0229	7.90	2.36	1.02	0.42	0.63
0.0247	14.54	1.23	1.51	0.57	0.85
0.0223	22.86	2.44	2.50	0.72	1.08
0.0235	40.0	1.30	3.11	0.94	1.41
0.0235	52.1	1.90	3.29	1.08	1.62

* With ζ at 30 mV and no electro-osmose.

† With ζ at 30 mV and electro-osmose.

the ζ -potential to be 30 mV (Street 1956), and the ionic concentrations from the filtrate conductivity values as CaCl_2 , MgCl_2 , or HCl as the case may be.

The results calculated according to Fricke and Curtis, particularly as presented in Table 3, show the random variation of these values; this tendency was repeated throughout all the measurements taken.

TABLE 4
H-KAOLINITE: ζ -POTENTIAL—FILTRATE CONDUCTIVITY

K_1 (ohm ⁻¹ cm ⁻¹ $\times 10^{-5}$)	ζ (mV)	K_1 (ohm ⁻¹ cm ⁻¹ $\times 10^{-5}$)	ζ (mV)
0.15	-32.5	0.53	-32.9
0.40	-32.9	0.64	-46.7
0.44	-34.2	1.49	-39.1
0.52	-39.6		

Since these measurements indicated that there was a reasonable degree of agreement in the order of magnitude of the measured (using F_1) and calculated (from ζ) values of the surface conductance of Ca-kaolinite plus CaCl_2 , it was felt that careful measurements should be made of the surface conductance of

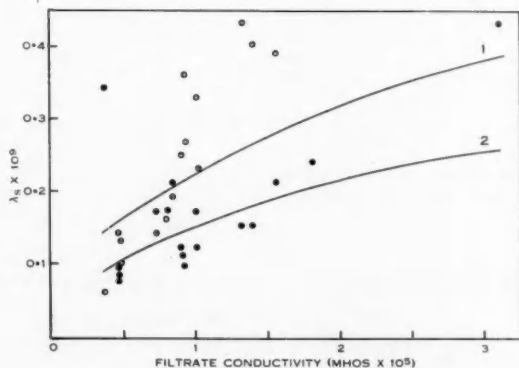


Fig. 2.—Surface conductivity-filtrate conductivity, Mg-kaolinite plus MgCl_2 .

○ Measured values (calculated with F_1). ● Measured values calculated with Fricke and Curtis's equation (4). Curves are values calculated from $\zeta=30$ mV; curve 1 with electro-osmose, and curve 2 without electro-osmose.

hydrogen-kaolinite throughout its neutralization curve. The results, for various bases, are shown in Figures 4, 5, and 6. The ζ -potentials used in these calculations are shown in Figure 7 and were calculated from measurements of electrophoretic velocity carried out in a microelectrophoresis cell (Street 1956), the

values are corrected for the relaxation effect according to the method of Stiger and Mysels (1955). The ionic concentrations used in the calculations were

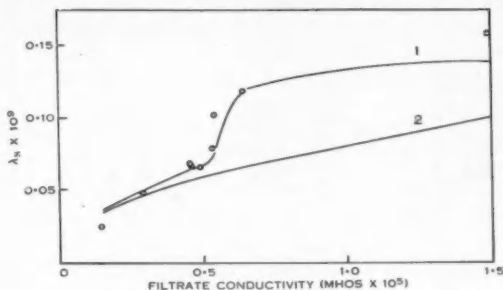


Fig. 3.—Surface conductivity-filtrate conductivity H-kaolinite plus HCl.

○ Measured values (F_1). Curve 1 is calculated from measured ζ (Table 4). Curve 2 is calculated from $\zeta=30$ mV. Both curves include the electro-osmotic contribution.

derived from conductivity and potentiometric titrations of these suspensions by the following method. From the pH curve the concentration of either H^+

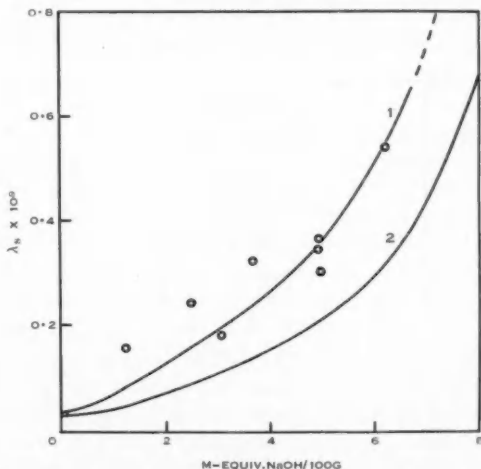


Fig. 4.—Surface conductivity-filtrate conductivity H-kaolinite plus base NaOH. Curves are values calculated from ζ (Fig. 7), curve 1 with electro-osmose and curve 2 without electro-osmose.

or OH^- was calculated at each addition of base, then the contribution to the conductivity to be expected from either H^+ plus HCO_3^- , or the particular cation

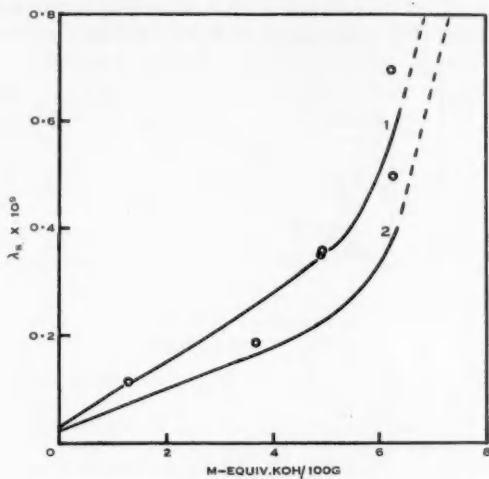


Fig. 5.—Surface conductivity-filtrate conductivity H-kaolinite plus base KOH. Curves are values calculated from ζ (Fig. 7). Curve 1 with electro-osmose and curve 2 without electro-osmose.

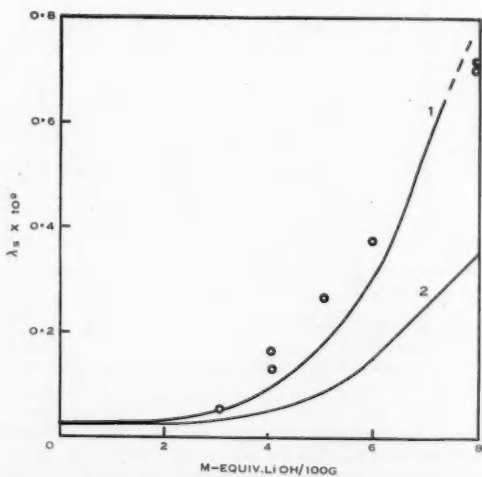


Fig. 6.—Surface conductivity-filtrate conductivity H-kaolinite plus base LiOH. Curves are values calculated from ζ (Fig. 7). Curve 1 with electro-osmose and curve 2 without electro-osmose.

plus OH^- was calculated; the excess of the measured value (of conductivity) over this calculated value was ascribed to the particular cation plus HCO_3^- . The ionic mobilities used were the weighted averages of those of the ionic species present at each measured point.

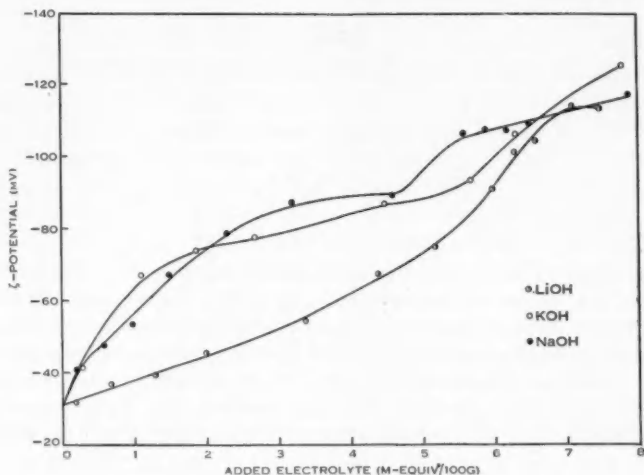


Fig. 7.— ζ -potential-added electrolyte (m-equiv/100 g).

V. DISCUSSION

The measurements are essentially exploratory and preliminary in nature; however, they do indicate that the calculated and measured surface conductances are at least of the same order of magnitude. The agreement between the calculated and measured values at low ionic concentrations suggests that more extensive measurements may show complete agreement.

The Fricke and Curtis equation (4) appears to give values in agreement with those calculated from ζ if the volume concentration of the particles is of the order of 0.025 or greater; if less than this it appears to vary randomly.

The choice of x , to be inserted in the modified Fricke equation (9) to obtain the factor F_1 necessary to calculate the value of conductance of solution, when present in the pores of the suspension, must be further investigated. With apparatus capable of very close temperature control, and of very accurate resistance measurements, then the differences of conductance between solution and suspension when the solution is very concentrated (i.e. surface conductance zero) can be investigated. Then $F_1 = K_1/K$ and at known ϕ , x can be evaluated from (9). Figure 8 shows how this determination can be used as a measure of the axial ratios of the particles concerned. Table 5 gives results obtained in the present investigation at high electrolyte concentration and used to calculate x , that is, the assumption of zero surface conductance has been made.

It is not certain that the surface conductance has reached zero at these concentrations; however, it was definite that above these values the resistance measurements were untrustworthy and the equation thus inapplicable. Without further investigation it is not possible to say to what concentration the surface conductance effect is noticeable.

TABLE 5
AXIAL RATIOS CALCULATED FROM CONDUCTANCE MEASUREMENTS

Electrolyte		K_1	K	a	$\frac{a}{b}$
		(ohm ⁻¹ cm ⁻¹ × 10 ⁻⁵)	(ohm ⁻¹ cm ⁻¹ × 10 ⁻⁵)		
KOH	47.4	43.4	0.276	16.5
NaOH	15.4	14.0	0.241	19.0

The question as to whether or no the electro-osmotic effect is active at this frequency (1000 cycles) of measurement cannot be resolved since the accuracy is not sufficient to do more than suggest that the order of magnitude of the measured and calculated surface conductance is the same, regardless of whether they are calculated with or without the electro-osmotic effect. In regard to this matter Svedberg and Anderson (1919) suggest that there is no electro-osmotic effect if the measurements are conducted at 1000 cycles or greater.

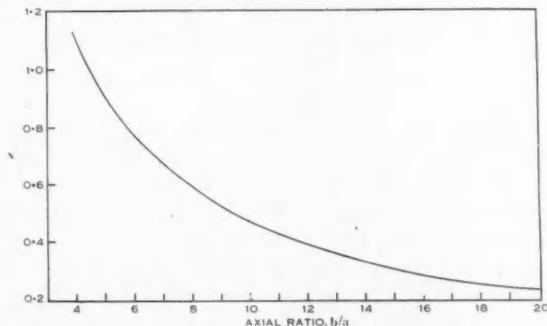


Fig. 8.—X-axial ratio.

There appears to be reasonable agreement between the calculated (with electro-osmose) and the measured values for hydrogen-kaolinite plus alkali; however, this may be illusory since (i) the applicability or otherwise of the electro-osmose correction is not known and (ii) if the kaolinite particles have both positive and negative areas on their surface (Schofield and Samson 1954), then, since the ζ -potential is the resultant of these, the measured surface conductance should be greater than that calculated from the measured ζ -potential.

Another factor to be considered is that pointed out by Henry (1948), namely, that the measured conductivity of a suspension will be compounded

of that of the solution plus surface conductance of the particles, together with the conductance of the particles themselves as a consequence of their ζ -potential. This will have a magnitude of

$$K_p = 1.5 \times 10^{-13} \rho \zeta^2 \cdot f(\kappa a) \cdot (1 + \kappa a)/a^2,$$

where K_p is this conductance, and the ζ -potential is in volts; and $\kappa = (4\pi e^2 \sum n_i z_i^2 / DkT)^{1/2}$, n_i = concentration in ions/c.c. of ions of species i and valency z_i , a plot of $f(\kappa a)$ against κa is available in Henry's (1948) paper.

This conductance will only have a serious effect on the results when the particle radius is small, and the ζ -potential is large. For NaOH at 7.44 m-equiv/100 g of kaolinite the ζ -potential is 0.117 V, thus with $a = 0.15 \times 10^{-4}$ cm, then $K_p = 0.243 \times 10^{-5}$ ohm $^{-1}$ cm $^{-1}$. Thus $K_p/K_1 = 0.032$, and $(K - K_1)/K_1 = 0.18$. The surface conductance calculated allowing for this effect is 1.88×10^{-9} ohm $^{-1}$, whilst that calculated without allowance is 2.33×10^{-9} ohm $^{-1}$.

The best that can be said at present then of these measurements is that the orders of magnitude of the measured and calculated values are the same at low ionic concentration, so that it would appear to be unnecessary to look for other sources of surface conductance as suggested by Overbeek (Kruyt 1952). This being so then further investigation of the surface conductance of kaolinite and other clay minerals is well justified. The correlation of these with measured ζ -potentials should further add to an understanding of the double layer processes.

VI. ACKNOWLEDGMENT

The author wishes to thank Dr. A. S. Buchanan of the Chemistry Department, University of Melbourne, for much practical assistance and many helpful discussions.

VII. REFERENCES

- ARCHIE, G. E. (1942).—*Trans. Amer. Inst. Min. (Metall.) Engrs.* **146**: 54.
 BIKERMAN, J. J. (1933).—*Z. Phys. Chem. A* **163**: 378.
 BIKERMAN, J. J. (1935).—*Kolloidschr.* **72**: 100.
 BIKERMAN, J. J. (1940).—*Trans. Faraday Soc.* **36**: 154.
 BOOTH, F. (1948).—*Trans. Faraday Soc.* **44**: 955.
 COLE, K. S. (1933).—*Cold Spr. Harb. Symp. Quant. Biol.* **1**: 23.
 FRICKE, H. (1924).—*Phys. Rev.* **24**: 575.
 FRICKE, H., and CURTIS, H. J. (1936).—*J. Phys. Chem.* **40**: 715.
 HENRY, D. C. (1931).—*Proc. Roy. Soc. A* **133**: 106.
 HENRY, D. C. (1948).—*Trans. Faraday Soc.* **44**: 1021.
 KRUYT, H. R. (1952).—"Colloid Science," Vol. 1. p. 235. (Elsevier Publ. Co. Inc.: Amsterdam.)
 MAXWELL, C. (1904).—"Electricity and Magnetism." 3rd Ed. Vol. 1. (Clarendon Press: Oxford.)
 O'CONNOR, D. J., STREET, N., and BUCHANAN, A. S. (1954).—*Aust. J. Chem.* **7**: 245.
 OVERBEEK, J. TH. G. (1943).—*Kolloidbeihfte* **54**: 287.
 SCHOFIELD, R. K., and SAMSON, H. R. (1954).—*Disc. Faraday Soc.* **18**: 135.
 SLAWINSKI, A. (1926).—*J. Chim. Phys.* **23**: 710.

- STIGER, D., and MYSELS, K. J. (1955).—*J. Phys. Chem.* **59**: 45.
- STREET, N. (1956).—Thesis, University of Melbourne.
- SVEDBERG, TH., and ANDERSON, H. (1919).—*Kolloidzchr.* **24**: 156.
- URBAN, F., WHITE, H. L., and STRASSNER, E. A. (1935).—*Colloid Symp. Annu.* p. 179.
- WINSAUER, W. O., and MCCARDELL, W. M. (1953).—*Trans. Amer. Inst. Min. (Metall.) Engrs. (Petrol. Branch)* **198**: 129.
- WINSAUER, W. A., SHEARIN, H. M., JR., MASSON, P. H., and WILLIAMS, M. (1952).—*Bull. Amer. Ass. Petrol. Geol.* **36**: 253.
- WYLLIE, M. J. R., and GREGORY, A. R. (1953).—*Trans. Amer. Inst. Min. (Metall.) Engrs. (Petrol. Branch)* **198**: 103.

OXIDATION REACTIONS IN MONOLAYERS OF LONG-CHAIN UNSATURATED COMPOUNDS

By A. R. GILBY* and A. E. ALEXANDER†

[Manuscript received October 18, 1955]

Summary

The kinetics of the oxidation of long-chain unsaturated compounds when spread as monolayers on KMnO_4 solutions has been determined from measurements of the changes in area with time. The effects of number of double bonds (unconjugated), of chain length, and of permanganate concentration were studied, as well as the behaviour of the dihydroxy compounds believed to be the first stage of the oxidation process.

The velocity constant has been found to increase markedly for each additional double bond, and to be independent of chain length, thus providing a quantitative measure of degree of unsaturation in unconjugated long-chain compounds.

Mixed films of unsaturated and dihydroxy acids have been studied and the results used to allow for deviation from additivity of areas in the reacting systems. On this basis the overall area-time curve, which goes through a maximum, has been quantitatively accounted for.

I. INTRODUCTION

During the study of the long-chain compounds present in insect cuticular waxes the determination of degree of unsaturation became of considerable importance. Preliminary work indicated the value of surface techniques, in which a monolayer is subjected to oxidation by dilute permanganate. To assist in the interpretation of the results a study was made using pure unsaturated compounds under identical conditions. The kinetics of oxidation of these pure compounds is discussed here, the biological applications being reported separately.

The oxidation of unsaturated long-chain compounds by dilute acid permanganate has been studied earlier by Hughes and Rideal (1933), Marsden and Rideal (1938), and Mittelman and Palmer (1942). The kinetics of the reaction can be obtained from the changes in surface area A , surface pressure π , or surface potential ΔV , depending upon the technique adopted. Since the reaction is frequently very sensitive to molecular orientation it is preferable to study the process at constant surface pressure and more convenient to utilize the area rather than the potential changes.

When a monolayer of oleic acid or compound of similar type is spread on dilute acid KMnO_4 the area (at constant π) first increases with time, reaches a maximum, and then decreases. The initial increase is attributed to the forma-

* School of Applied Chemistry, N.S.W. University of Technology, Broadway, Sydney; present address: Division of Entomology, C.S.I.R.O., Canberra, A.C.T.

† School of Applied Chemistry, N.S.W. University of Technology, Broadway, Sydney.

tion of the dihydroxy acid (Hilditch 1926), the $-\text{OH}$ groups added across the double bond giving an additional point of attachment to the surface and so increasing the area. Subsequently, further oxidation occurs at this point with ultimate fission and formation of two carboxyl groups. The two resulting small molecules are usually soluble and disappear from the film. In the case of $\alpha\beta$ -isoleic acid, one of the final fragments is not soluble and is recognizable as palmitic acid from its surface behaviour (Hughes and Rideal 1933).

Hitherto, very little attention has been paid to the second part of the reaction in which the film slowly disappears from the surface. In their study of the oxidation of triolein monolayers, Mittelman and Palmer (1942) found that the disappearance of the film did not follow a simple first order law, and suggested that the product of the first reaction may not be entirely the $-\text{CH}(\text{OH})\text{CH}(\text{OH})$ -compound but partly, say, a peroxide which could subsequently polymerize. However, it will be shown here that such additional postulates are unnecessary even for a quantitative treatment of the complete reaction.

The monolayer oxidation on KMnO_4 of compounds with more than one double bond had been previously studied only in conjugated systems. These monolayers are autoxidized even on pure water; in the presence of KMnO_4 they split into readily soluble fragments at a rate too rapid to measure, for example, α - and β -elaeostearic acids (Hughes and Rideal 1933). With the unconjugated systems studied here the reaction velocity has been found to increase markedly with the degree of unsaturation, a finding which may be of value for analytical purposes.

II. EXPERIMENTAL

All the compounds investigated were *cis*-isomers. With the exception of oleyl alcohol, a purified sample obtained from Lever Bros., all the unsaturated and dihydroxy compounds were kindly supplied by Dr. H. H. Hatt, Division of Industrial Chemistry, C.S.I.R.O. The oleic acid, methyl linoleate, and methyl linolenate were particularly pure compounds originating from the Hormel Foundation, University of Minnesota, U.S.A. A list of the compounds is given in Table 1.

The liquid unsaturated compounds were sealed under vacuum and kept in the dark at 0°C . After solutions were made up for use, they were kept under nitrogen at 0°C , and, particularly the poly-unsaturated compounds, used as soon as possible.

Solutions for spreading were made up in purified benzene containing 1 per cent. ethyl acetate, or in redistilled light petroleum (b.p. 60 – 80°C). With the dihydroxy acids a mixture of 80 per cent. benzene-20 per cent. ethanol was used.

Films were spread directly onto the substrate of acid permanganate ($0.01\text{N H}_2\text{SO}_4$) freshly made up from solid AnalaR KMnO_4 .

The film balance used was a simple manual type (Alexander 1947). After cleaning the trough in the usual way the monolayer was spread 3 or 4 sec before

zero time. The film was then compressed until a pressure of 5 dyne cm^{-1} was developed. This was achieved some 20 sec after the film was spread, so that the beginning of the reaction was somewhat indefinite. The pressure was kept constant and readings of the area and the surface potential taken with time, usually over some 4–5 hr, beyond which it was considered that the risk of contamination would invalidate further measurements. In duplicate experiments, replication was better than ± 2.5 per cent. During each run, the temperature of the air and the solution was maintained at $25 \pm 1^\circ \text{C}$ by means of an electrical heater in the balance case.

TABLE 1
COMPOUNDS EXAMINED

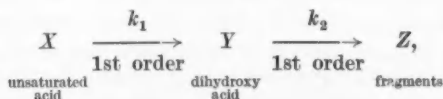
Compound (<i>cis</i> -isomers)	Structure
C_{18} Chain length	
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, m.p. 13.3°C
Methyl linoleate	$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CH}.\text{CH}_2.\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOCH}_3$
Methyl linolenate	$\text{CH}_3.\text{CH}_2.\text{CH}:\text{CH}.\text{CH}_2.\text{CH}:\text{CH}.\text{CH}_2.\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOCH}_3$
Oleyl alcohol	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}$
9,10-Dihydroxyoctadecanoic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{OH}).\text{CH}(\text{OH}).(\text{CH}_2)_7\text{COOH}$, m.p. $93.4\text{--}94.0^\circ \text{C}$
C_{20} Chain length	
11,12-Dihydroxyeicosanoic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{OH}).\text{CH}(\text{OH}).(\text{CH}_2)_5\text{COOH}$, m.p. $96.8\text{--}97.4^\circ \text{C}$
C_{22} Chain length	
Erucic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOH}$, m.p. $33.0\text{--}33.5^\circ \text{C}$
Methyl erucate	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOCH}_3$
13,14-Dihydroxydocosanoic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{OH}).\text{CH}(\text{OH}).(\text{CH}_2)_{11}\text{COOH}$, m.p. $99.6\text{--}100.4^\circ \text{C}$

With the permanganate solutions, stable potentials could not be obtained with the Ag/AgCl electrode dipping directly into the solution but this was overcome by use of a bridge containing 0.01N H_2SO_4 .

(a) *The Evaluation of Velocity Constants*

The overall reaction will be treated as two consecutive reactions, it being assumed that the oxidation proceeds via the dihydroxy compound.

The simplest case arises when both processes are kinetically of the first order, namely,



where k_1 and k_2 are the two velocity constants.

The concentrations of X , Y , and Z at time t , can then be calculated in terms of the initial concentration of X , X_0 , and the constants k_1 and k_2 (Esson 1866)

$$X = X_0 e^{-k_1 t}, \quad \dots\dots\dots (1)$$

$$Y = \frac{X_0 k_1}{k_1 - k_2} (e^{-k_1 t} + e^{-k_2 t}), \quad \dots\dots\dots (2)$$

$$Z = X_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]. \quad \dots\dots\dots (3)$$

There are only a limited number of instances where both k_1 and k_2 are known. The most thorough application has been in the radioactive series, where equations have been obtained expressing the total activity at any time (Cook and Duncan 1952). These equations are not suitable to monolayer reactions.

The problem of obtaining the rate constants k_1 and k_2 from a set of experimental data has not been satisfactorily solved. However, in special cases not applicable here adequate solutions have been obtained (e.g. Swain 1944; Klein and Fagley 1954; see also Hitchcock and Robinson 1952).

Where consecutive reactions of order higher than the first are involved, the equations become extremely complicated and approximate methods have to be employed.

If the oxidation of the unsaturated compound to the dihydroxy derivative follows a first order law, and assuming molecular areas to be additive, the usual equation for a first order reaction may be written, that is,

$$\frac{A - A_\infty}{A_0 - A_\infty} = e^{-kt}, \quad \dots\dots\dots (4)$$

where A_0 is the initial area per molecule, A_∞ is the final area per molecule, A is the area per molecule at time t , and k is the rate constant. Hence k may be evaluated from the slope of the $\log (A - A_\infty)$ v. t curve. Three interpretations of this method will be considered.

Previous workers have used equation (4) to determine k , taking $A_\infty = A_{\max.}$, where $A_{\max.}$ is the maximum value of the area attained during the oxidation (method 1). However, as pointed out by Guggenheim (1926) this method of determining k (from eqn. (4)) weights the value of A_∞ unduly. The method developed by Guggenheim as applied to the present example would consist in plotting $\log (A' - A)$ against t , where A is the area at time t , whilst A' is the area at a constant time interval after the reading A . If the reaction is first order, then a straight line will be obtained having the slope $-k \log e$ (method 2).

Although a set of results may be so treated, the value obtained is not the true rate constant characterizing the oxidation of the double bonds because the effect of the decreasing reaction is being ignored (see below). To obtain the true rate constant the appropriate value of A_∞ is that occupied under identical conditions by the corresponding dihydroxy compound and it will be shown below that this value of A_∞ is very different from $A_{\max.}$ (method 3).

Turning now to the decreasing reaction, if this is a simple first order process, equation (4) will again apply. If the value of A_{∞} is zero, as it would be expected to be if all the fragments are rapidly and completely soluble, equation (4) becomes

$$A = A_0 e^{-kt}, \dots\dots\dots (5)$$

and k may be obtained from a plot of $\log A$ v. t . If A_{∞} is not zero, Guggenheim's method may still be applied.

(b) *Interactions in the Mixed Films*

Once the monolayer consists appreciably of two components, any interactions between them will invalidate the assumption of additivity of areas, on which the above treatment has been based. Calculations, using equations (1) and (2) for oleic acid and equations (1) and (14) for erucic acid, show that even after prolonged periods of oxidation there is still an appreciable proportion of unsaturated acid in the film and conversion to dihydroxy acid is by no means complete at the end of the "increasing" reaction (see Table 2).

TABLE 2
FRACTION (F) OF UNSATURATED ACID IN FILM DURING OXIDATION
0.0001N KMnO_4 ; 0.01N H_2SO_4 ; temp. = 25 °C; $\pi = 5$ dyne cm^{-1}

t (min)	10	20	40	80	85
F oleic	0.91	0.80	0.70	0.58	
F erucic	0.89	0.80	0.64		0.37
t (min)	120		180	240	360
F oleic	0.50		0.42	0.39	0.31
F erucic	0.24		0.12	0.06	

Three important consequences follow. Firstly, it cannot be expected that the A v. t curves for the decreasing reaction of an unsaturated acid will analyse kinetically to agree with the oxidation of the pure hydroxy acid even late in the reaction. This would also account for the fact that the decreasing curves for unsaturated acids do not give a linear $\log A$ v. t plot. It is of interest to note that this situation would apply to the work of Mittelman and Palmer (1942) mentioned earlier. Their assumption that the product of the first oxidation of triolein is not homogeneous would, therefore, appear unnecessary. Secondly, rate constants of the increasing reaction of the oxidation of unsaturated compounds calculated by taking A_{max} as A_{∞} should not be interpreted as the true values for the formation of dihydroxy compounds. Thirdly, any interactions between the components of the mixed film giving rise to departures from ideality will establish themselves early in the reaction and persist throughout.

If factors, such as accessibility to the surface, affecting the mechanism of the reaction are involved, it would be expected that once the experimental curve began to deviate from the ideal equation, the deviation would be permanent. On the other hand, if interactions cause, for example, non-additivity in the areas

occupied by each molecule in the mixed film whilst not altering the other factors, then the reaction would be expected to follow closely the ideal equation both before appreciable dihydroxy acid had built up and after the unsaturated acid had reached small proportions. The second type of behaviour occurs here.

III. RESULTS AND DISCUSSION

An experimental study was undertaken to test whether the areas occupied in mixed films are additive. Mixtures of oleic acid with its dihydroxy derivative and erucic acid with its dihydroxy compound were made up in varying ratios and determined at a pressure of 5 dyne cm^{-1} . The results are shown in Figure 1. Considerable departures from ideality are indicated, the curves being reminiscent of the vapour pressure curves given by binary mixtures exhibiting positive

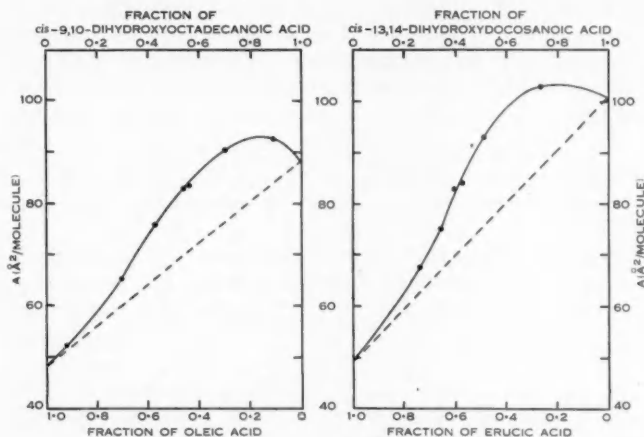


Fig. 1.—Variation of molecular area A with composition for unsaturated acid-dihydroxy acid mixtures. 0.01N H_2SO_4 ; $\pi = 5$ dyne cm^{-1} ; temp. = 25 °C.

deviations from Raoult's law. This similarity is not surprising as the causes of positive deviations from Raoult's law, namely, differences in polarity and the attractive forces between molecules, are amongst the factors governing the area occupied by a molecule in a monolayer. The application of these corrections to the specific cases of oleic and erucic acids will be given later.

The kinetic results obtained in the various oxidations are given in Figures 2–7 and in view of the relatively small changes in surface potential which occur during a number of the reactions, all velocity constants have been calculated from the changes in area. The whole reaction of an unsaturated compound will be divided into the increasing reaction (i.e. up to A_{max}) and the decreasing reaction (i.e. from A_{max} to the final value which is frequently zero).

Further since dihydroxy compounds are the probable intermediates in the oxidation the behaviour of a number on dilute permanganate was also studied.

(a) Dihydroxy Compounds

The results are shown in Figures 2-4. In each case there is a small increase in surface potential as the oxidation proceeds. The known contribution of each hydroxyl group in this type of compound to the surface moment is approximately 160 millidebye units (mD) compared with 180 mD for a carboxyl group (Goddard and Alexander 1950). Thus, if each hydroxyl group is replaced by a carboxyl group during the oxidation, other conditions remaining the same, only a small increase in surface potential would be expected. The same behaviour occurs during the decreasing reaction in the oxidation of unsaturated compounds.

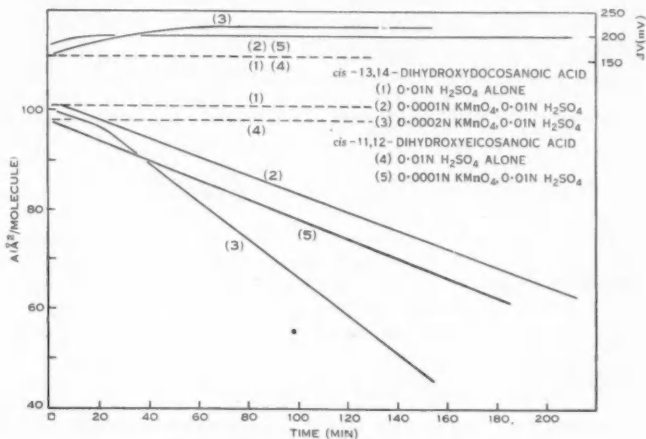


Fig. 2.—Monolayer oxidations by dilute KMnO_4 , $\pi = 5 \text{ dyne cm}^{-1}$; temp. = 25°C .

The rate constants calculated from the area-time relationships are summarized in Table 3. These will be discussed in three sections.

(i) C_{22} and C_{20} Acids, Very Dilute KMnO_4 .—The experimental results are given in Figure 2. Both acids are quite insoluble on 0.01N H_2SO_4 alone. On dilute permanganate, a relatively slow reaction occurs. The area-time curves are linear, that is, the reactions are of zero order with respect to film concentration. On 0.0002N KMnO_4 there appears to be an initial induction period when the reaction is not zero order. The zero order rate is proportional to the bulk permanganate concentration (Table 3).

If the reaction were genuinely zero order with respect to the film reactant, the consequences would be difficult to accept. However, it could be that the area of the film is not a true measure of the dihydroxy acid and the observed area-time curve could arise if the oxidation fragments remain sufficiently long in the film to expand the monolayer.

This interpretation is supported by experiments in which the oxidation fragments of erucic acid, both alone and as mixtures with erucic acid, were

spread on 0.01N H_2SO_4 . Azelaic acid, $COOH.(CH_2)_{11}.COOH$, was extremely rapidly soluble whilst it could scarcely be detected when spread as 10 per cent. of a mixture with erucic acid. In contrast, the other fragment, pellargonic acid, $CH_3.(CH_2)_7.COOH$, did not dissolve nearly as rapidly either alone or mixed with erucic acid. Mixed films took several minutes to contract to the area of erucic acid. Hence, the slow dissolution of pellargonic acid from the oxidizing film is considered to be the cause of the apparent zero order reaction. No quantitative measurements could be made of the rate of solution which would have enabled allowance to be made for the effect on the experimental curve.

TABLE 3
RATE CONSTANTS OF THE OXIDATION OF DIHYDROXY ACIDS
0.01N H_2SO_4 ; temp.=25 °C; $\pi=5$ dyne cm^{-1}

Acid	KMnO ₄ Concn.				
		0	0.0001N	0.0002N	0.05N
<i>cis</i> -9,10-Dihydroxyoctadecanoic* ..		$k_{uni.} (min^{-1})$ 0.006	0.013	0.021	0.062
<i>cis</i> -11,12-Dihydroxyeicosanoic ..		$k_{zero} (A^2 min^{-1})$ 0	0.21		
<i>cis</i> -13,14-Dihydroxydocosanoic ..		0	0.19	0.39	0.062

* The k values for this compound also include a contribution from the solution of the parent molecule.

(ii) C_{18} Acid, Very Dilute $KMnO_4$.—The C_{18} dihydroxy acid monolayer is quite rapidly soluble on water alone. The behaviour on the various substrates is shown in Figure 3.

The curves accurately follow a first order law when treated by Guggenheim's method. A plot of $\log A$ v. t is also linear, hence A_∞ must be zero. The first order rate constants, given in Table 3, are a linear function of the permanganate concentration.

In these systems the first order process of solution of the dihydroxy acid is occurring simultaneously with the oxidation reaction, and an attempt was made to separate the two processes by subtracting the curves. However, it could not be concluded that the oxidation contribution was of zero order. Thus, unlike the previous case, the expanding effect of the fragments is not experimentally detectable. It may be noted that the rate constant on 0.0001N $KMnO_4$ is approximately twice that calculated for the decreasing reaction of oleic acid (see Table 5). Agreement could be expected only if conversion of the double bonds to dihydroxy compounds were complete at least by the early stages of the decreasing reaction and it has been shown above that this is not so.

(iii) $0.05N$ $KMnO_4$.—Both dihydroxy acids studied show the same type of curve (Fig. 4), the longer-chain acid occupying the larger areas, and in contrast to the unsaturated acids they initially occupy their normal areas.

After about 40 min reaction the curves follow a first order law, rate constants calculated by Guggenheim's method being given in Table 3. These values agree reasonably with those for oleic and erucic acids in Table 5. In the earlier

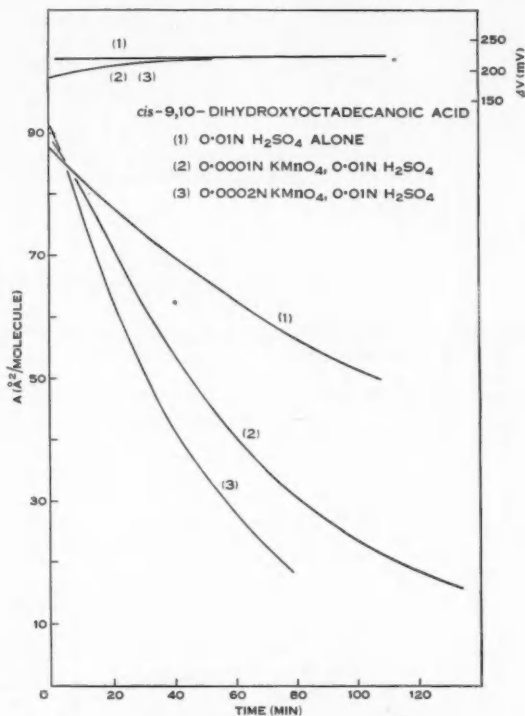


Fig. 3.—Monolayer oxidations by dilute $KMnO_4$.
 $\pi = 5$ dyne cm^{-1} ; temp. = $25^\circ C$.

part of the reaction it is likely that a similar effect to that giving rise to the pseudo-zero order reaction on more dilute permanganate is occurring although more accentuated.

The agreement between the first order constants of the dihydroxy acids and the decreasing reaction of the unsaturated acids (see below) suggests that, at this stage, conditions are similar in both cases. Compared with the reaction on more dilute permanganate, the complete elimination of double bonds is over in a relatively short time, and the curves then become similar to the dihydroxy acids alone.

(b) *Unsaturated Acids*

Before considering the various reactions in more detail, there are several qualitative conclusions which can be made.

(i) The similarity in the oxidation curves of oleic acid and oleyl alcohol in Figure 5. These two substances have almost identical force-area curves and it would be expected that the double bonds would be virtually equally accessible to the surface at the same pressure.

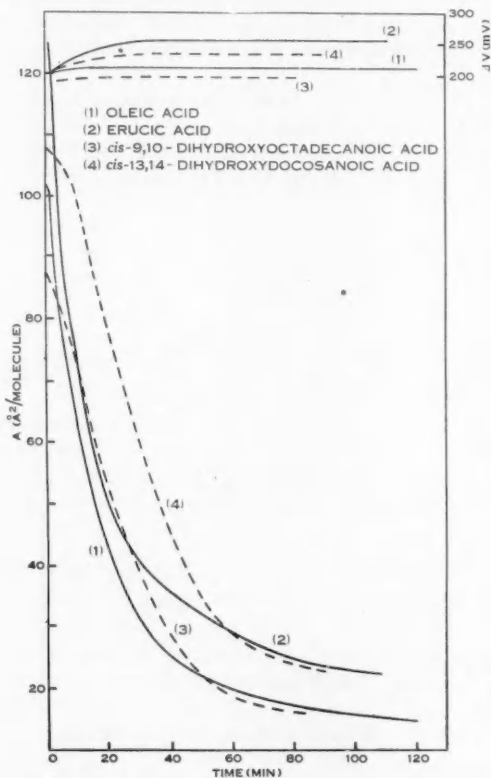


Fig. 4.—Monolayer oxidations by 0.05N KMnO_4 , 0.01N H_2SO_4 .
 $\pi = 5 \text{ dyne cm}^{-1}$; temp. = 25 °C.

(ii) The marked contrast in behaviour between compounds with one, two, and three double bonds in Figures 6 and 7. On 0.0001N KMnO_4 the increasing reaction is complete in a few minutes with methyl linoleate and almost instantaneously with methyl linolenate, compared with 1 hr for oleic acid. On 0.05N KMnO_4 , the increasing reaction is too rapid to follow whilst the dissolution reaction is faster the more double bonds there are in the molecule. Only the very end of the reaction can be followed with methyl linolenate.

(iii) The general similarity in the shape of the curves for C_{22} and C_{18} compounds as shown in Figure 5.

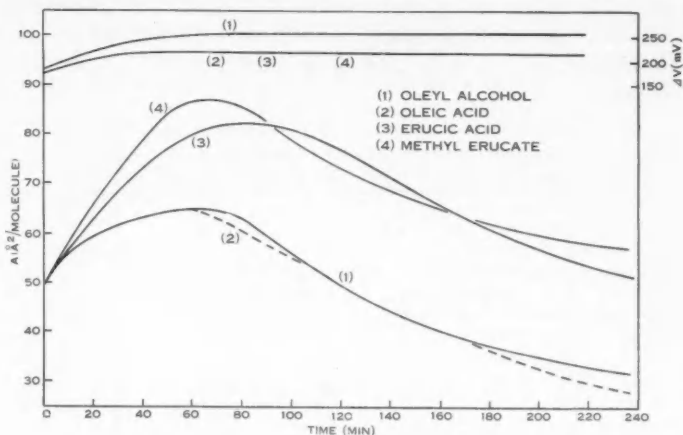


Fig. 5.—Monolayer oxidations by 0.0001N $KMnO_4$, 0.01N H_2SO_4 .
 $\pi = 5 \text{ dyne cm}^{-1}$; temp. = 25 °C.

(iv) An increase in surface potential occurs during the increasing reaction, whereas during the decreasing reaction it remains sensibly constant.

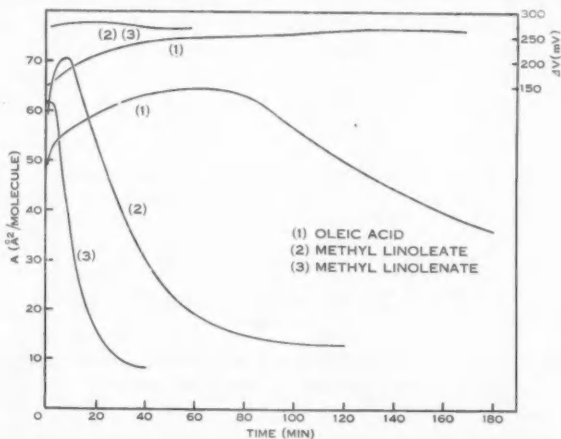


Fig. 6.—Monolayer oxidations by 0.0001N $KMnO_4$, 0.01N H_2SO_4 .
 $\pi = 5 \text{ dyne cm}^{-1}$; temp. = 25 °C.

(c) Quantitative Treatment

(i) *The Increasing Reaction.*—The experimental curves for the initial reaction have been analysed by the three methods outlined previously. The method of

least squares was used to fit straight-lines and the rate constants so found are given in Table 4. With methyl linolenate, the reaction was too fast to be measured. The curves for methyl erucate and erucic acid did not analyse for a first order law by Guggenheim's method although satisfactory constants could be obtained from the early parts of the curve (the first 30–40 min) by the other methods.

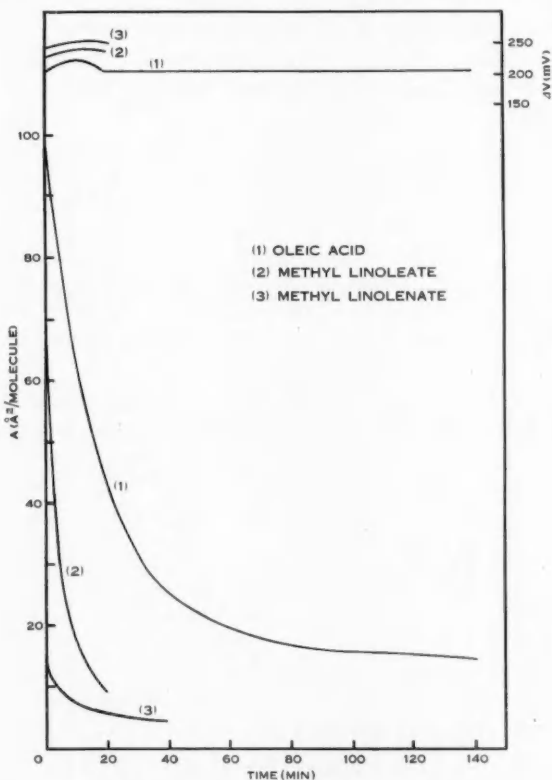


Fig. 7.—Monolayer oxidations by 0.05N KMnO_4 , 0.01N H_2SO_4 .
 $\pi = 5 \text{ dyne cm}^{-1}$; temp. = 25 °C.

The values obtained by the first two methods show fair agreement, whereas those from the third are considerably lower. As it is shown below that the experimental curves can be quantitatively explained on the assumption that the reactions proceed via the dihydroxy compounds, it is believed that the latter values are more nearly the true rate constants. The "true" rate constants for oleic acid and erucic acid are seen to be in fair agreement.

However, the rate constants calculated by the other methods are of the right order and may be used as a semiquantitative measure to indicate, for example, the large increase in the rate constant as the number of double bonds is increased and the small effect of altered chain length. The effect of ignoring the decreasing reaction is to give false high values of the apparent rate constant since the increasing reaction appears to be complete sooner than it actually is.

TABLE 4

FIRST ORDER RATE CONSTANTS FOR INCREASING REACTION
0.0001N KMnO_4 , 0.01N H_2SO_4 ; temp. 25 °C; $\pi=5$ dyne cm^{-1}

Compound	$k_{\text{unl.}} (\text{min}^{-1})$		
	Log $(A_{\text{max}} - A) v. t$ Method 1	Guggenheim's Method 2	Log $(A_{\text{dih}} - A) v. t$ Method 3
Oleic acid	0.044	0.039	0.010
Oleyl alcohol	0.046	0.039	
Methyl linoleate	0.60	0.58	
Methyl linolenate	v.r.*	v.r.	
Erucic acid	0.025	—	0.014
Methyl erucate	0.030	—	

* v.r., Too rapid to be measured.

(ii) *The Decreasing Reaction.*—(1) 0.0001N KMnO_4 . Since the beginning and end of the decreasing reaction are both uncertain, the only feasible method for analysing the results is that of Guggenheim. Excluding the beginning and the end of the decreasing reaction, it was possible in this way to obtain a first order rate constant for a number of compounds. These values are given in Table 5. None of the curves shows a linear log $A v. t$ plot.

TABLE 5

FIRST ORDER RATE CONSTANTS FOR DECREASING REACTION
0.01N H_2SO_4 ; temp. = 25 °C; $\pi=5$ dyne cm^{-1}

Compound	$k_{\text{unl.}} (\text{min}^{-1})$	
	0.0001N KMnO_4	0.05N KMnO_4
Oleic acid	0.007	0.06
Methyl linoleate	0.050	0.16
Methyl linolenate	0.13	v.r.*
Erucic acid	0.007	0.07

* v.r., Too rapid to be measured.

As for the increasing reaction, the results illustrate the greater rate of disappearance of the monolayer as the number of double bonds in the molecule is increased. Again, increase in chain length from C_{18} to C_{22} has no effect on the rate constant.

(2) $0.05N KMnO_4$. At this concentration of oxidizing agent, the increasing reaction is practically instantaneous (Figs. 4 and 7). First order rate constants can be calculated for the decreasing reactions and these are given in Table 5. A comparison of the different compounds shows similar relations to those on the more dilute permanganate.

Comparison of the two columns in Table 5 shows that, corresponding with a 500-fold increase in the permanganate concentration, there is only about a tenfold increase in the rate constant. Hence the chemical process is probably complete within a very short time and the rate of area reduction is then determined by the rate of dissolution of the various fragments. With methyl linolenate, where the fragments are extremely small, the whole process is very rapid.

(d) *Detailed Consideration of Oleic Acid*

The following assumptions are made:

- (i) The reaction consists of two consecutive first order reactions.
- (ii) Accessibility to the surface for reaction is not altered in the mixed film.
- (iii) The oxidation fragments Z rapidly dissolve from the film.
- (iv) The areas occupied by each molecule in the monolayer are additive.
(As shown earlier this is not so, but non-additivity is allowed for later in the present treatment.)

The total area of the film at any time depends on the molecular density of the unsaturated acid X and the dihydroxy acid Y . Since at a surface pressure of 5 dyne cm^{-1} the area per molecule occupied by oleic acid is 48\AA^2 , whereas the dihydroxy acid occupies 88\AA^2 , each molecule of oleic acid which reacts is replaced by a molecule occupying 1.8 times the area.

Therefore, since areas are assumed additive at constant surface pressure, the total area of the mixed film at any time is

$$A = X + 1.8Y, \dots\dots\dots (6)$$

provided A is given in $\text{\AA}^2/\text{molecule}$ calculated on the basis of the number of molecules of oleic acid spread at the beginning and both X and Y are given on a similar basis. Substituting from equations (1) and (2), equation (6) becomes

$$A = A_0 e^{-k_1 t} + \frac{1.8 A_0 k_1}{k_1 - k_2} (-e^{-k_1 t} + e^{-k_2 t}), \dots\dots\dots (7)$$

where A_0 , the initial area per molecule of oleic acid, is used to express its initial concentration. The values of k_1 and k_2 are independent of the units used to measure X , Y , and Z but do depend on the unit of time.

Differentiating equation (7) with respect to t ,

$$\frac{dA}{dt} = -A_0 k_1 e^{-k_1 t} + \frac{1.8 A_0 k_1}{k_1 - k_2} (k_1 e^{-k_1 t} - k_2 e^{-k_2 t}), \dots\dots\dots (8)$$

At the maximum in the area-time curve ($t = t_m$) $dA/dt = 0$.

Hence

$$t_m = \frac{2.303}{k_1 - k_2} \log \frac{0.8k_1 + k_2}{1.8k_2} \quad \dots \dots \dots (9)$$

From the oxidation of the pure dihydroxy acid the value of k_2 is 0.013 min^{-1} . Values of t_m calculated using this value of k_2 and different assumed values of k_1 in equation (9) are given in Table 6.

TABLE 6
 t_m VALUES CALCULATED FROM EQUATION (9)
 $k_2 = 0.013 \text{ min}^{-1}$

$k_1 \text{ (min}^{-1}\text{)}$	0.0001	0.001	0.01	0.02	0.045
$t_m \text{ (min)}$	44	46	35.6	33	14

The maximum value of t_m is about 45 min no matter how small the value of k_1 . The observed value of t_m is 55 min.

A further test can be made and the accuracy with which equation (7) describes the reaction considered. The value of k_1 calculated from the early part of the reaction and equation (4) with $A_\infty = 88 \text{ \AA}^2$ (corresponding to the dihydroxy acid) is 0.010 (Table 4). Using this value of k_1 and the value of k_2 from the pure dihydroxy acid, the values of A obtained from equation (7) are compared with experimental values in Table 7.

TABLE 7
OBSERVED, CALCULATED, AND CORRECTED AREAS OF MONOLAYERS DURING OXIDATION
0.0001N KMnO_4 ; 0.01N H_2SO_4 ; temp. = 25°C ; $\pi = 5 \text{ dyne cm}^{-1}$

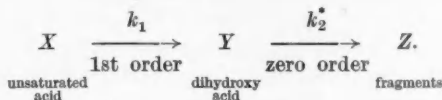
$t \text{ (min)}$	10	20	40	60	80	100	120	150	180	200	240	360
Oleic acid														
$A_{\text{obs.}}$	56	59	63	65	63	55	49	43	36	34	23	21
$A_{\text{calc.}}$	(eqn. (7))		54	55	56	56	51	46	42	34	29	25	18	8
$A_{\text{corr.}}$	(Fig. 1)	..	55	56	57	58	51	45	42	35	30	26.5	23	20
Erucic acid														
$A_{\text{obs.}}$	56	62	73	80	82.5	81	77	68	62	59	52	
$A_{\text{calc.}}$	(eqn. (16))		55.5	60	64.5	67	69	69	68	64	62	59	54	
$A_{\text{corr.}}$	(Fig. 1)	..	56	60	65	66	68	69	67	61	58	56	51	

Over a large part of the reaction, the experimental values differ appreciably from those calculated but these differences are reduced when correction is made for non-additivity of areas using the results of Figure 1 and Table 2. The corrected areas are shown in Table 7.

(e) Detailed Consideration of Erucic Acid

In this case the oxidation of the pure dihydroxy acid does not give a first order rate constant, the experimental rate being of zero order. Therefore, the

reaction will be treated as consisting of a first order reaction followed by one of zero order.



The concentration of X at time t is again given by equation (1). Using the same basic assumptions as in the earlier calculations the following treatment has been developed.

Let the amounts of Y and Z formed up to time t be y and z respectively, then

$$\frac{dy}{dt} = k_1(X_0 - y), \quad \dots \quad (10)$$

and

$$\frac{dz}{dt} = k_2^*, \quad \dots \quad (11)$$

Integration of equations (10) and (11), when $y=0$ and $z=0$ at $t=0$, gives respectively,

$$y = X_0(1 - e^{-k_1 t}), \quad \dots \quad (12)$$

and

$$z = k_2^* t. \quad \dots \quad (13)$$

Whence

$$y - z = Y = X_0(1 - e^{-k_1 t}) - k_2^* t. \quad \dots \quad (14)$$

Since each molecule of X (occupying 49\AA^2) which reacts yields a molecule of Y occupying double its area (101\AA^2) then the area of the film is given by

$$A = X + 2Y. \quad \dots \quad (15)$$

Substituting from equations (1) and (14), and since k_2 , the value of k_2^* (the zero order rate of disappearance of Y estimated from the oxidation of the dihydroxy acid) already includes this difference,

$$A = A_0 e^{-k_1 t} + 2A_0(1 - e^{-k_1 t}) - k_2 t,$$

where $k_2 = 2k_2^*$,

$$= 2A_0 - A_0 e^{-k_1 t} - k_2 t. \quad \dots \quad (16)$$

Differentiating equation (16)

$$\frac{dA}{dt} = k_1 A_0 e^{-k_1 t} - k_2. \quad \dots \quad (17)$$

Equating to zero, $t=t_m$ and solving for t_m ,

$$t_m = \frac{2.303}{k_1} \log \left(\frac{A_0 k_1}{k_2} \right). \quad \dots \quad (18)$$

The observed value of k_1 , calculated on the early part of the reaction from the first order law as previously with $A_\infty = 101 \text{ \AA}^2$, is 0.014. Using the value $k_2 = 0.19$ derived from the oxidation of the pure dihydroxy acid and substituting for k_1 and k_2 in equation (18), the calculated value for the time of the maximum is $t_m = 88 \text{ min}$, in very close agreement with the experimental value of 85 min.

Unlike equation (7), equation (16) may readily be solved for k_1 if A , k_2 , and t are known. Values so obtained for k_1 are of the same order as the experimentally determined values. Alternatively, the values of the area at various times may be calculated from equation (16) using the values of k_1 and k_2 found experimentally. This has been done in Table 7. There is seen to be good agreement between calculated and observed areas during the initial and final parts of the reaction but some discrepancy in the intermediate stages.

IV. CONCLUSION

The theoretical results given here were calculated on the assumption that the monolayer oxidation of long-chain unsaturated compounds on dilute potassium permanganate proceeds first by the formation of a dihydroxy compound at the double bond which then, by subsequent oxidation, splits to smaller soluble products. Although the equations closely describe the experimental curves when suitably corrected, this does not prove unequivocally that the assumed mechanism is correct since, as always in reaction kinetics, alternative mechanisms may give equally good agreement. However, the present work provides very strong evidence that the oxidation does proceed as described.

V. ACKNOWLEDGMENTS

The authors wish to thank Dr. D. F. Waterhouse, and Dr. R. H. Hackman, both of the Division of Entomology, C.S.I.R.O., for their interest and assistance in this research project. At various periods during the work, one of us (A.R.G.) has received financial assistance from I.C.I.A.N.Z. (Fellowship), the Dafydd Lewis Trust (Scholarship), and C.S.I.R.O. (Grant). This help is gratefully acknowledged.

VI. REFERENCES

- ALEXANDER, A. E. (1947).—*Nature* **159** : 304.
COOK, G. B., and DUNCAN, J. F. (1952).—"Modern Radiochemical Practice." (Clarendon Press : Oxford.)
ESSON, W. (1866).—*Phil. Trans. Roy. Soc. Lond.* **156** : 220.
GODDARD, E. D., and ALEXANDER, A. E. (1950).—*Biochem. J.* **47** : 331.
GUGGENHEIM, E. A. (1926).—*Phil. Mag.* (7) **2** : 538.
HILDITCH, T. P. (1926).—*J. Chem. Soc.* **1926** : 1828.
HITCHCOCK, F. L., and ROBINSON, S. M. (1952).—"Differential Equations in Applied Chemistry." 2nd Ed. p. 60. (John Wiley & Sons : New York.)
HUGHES, A. H., and RIDEAL, E. K. (1933).—*Proc. Roy. Soc. A* **140** : 253.
KLEIN, E., and FAGLEY, T. F. (1954).—*J. Phys. Chem.* **58** : 447.
MARSDEN, J., and RIDEAL, E. K. (1938).—*J. Chem. Soc.* **1938** : 1163.
MITTELMANN, R., and PALMER, R. C. (1942).—*Trans. Faraday Soc.* **38** : 506.
SWAIN, C. G. (1944).—*J. Amer. Chem. Soc.* **66** : 1696.

THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

II. ETHANOL AND ISOPROPANOL SYSTEMS

By I. BROWN,* W. FOCK,* and F. SMITH*

[Manuscript received March 16, 1956]

Summary

New experimental data are given for the heats of mixing of the systems ethanol+toluene at 35 °C, ethanol+methylcyclohexane at 35 °C, and *iso*-propanol+benzene at 45 °C and for the liquid-vapour equilibrium data for the latter system at 45 °C.

These data have been used together with previously published data to calculate the excess free energy, heat and excess entropy of mixing at even mole fractions for the above systems. These functions have also been calculated from published data for the systems ethanol+benzene at 45 °C and ethanol+2,2,4-trimethylpentane at 25 °C.

I. INTRODUCTION

The present work forms part of a programme of measurement of the thermodynamic properties of alcohol solutions. Data for the system ethanol+carbon tetrachloride have been given in Part I of this series by Barker, Brown, and Smith (1953) and by Brown and Fock (1955).

II. APPARATUS AND METHODS

Heats of mixing for the systems ethanol+benzene and ethanol+2,2,4-trimethylpentane were measured previously by Brown and Fock (1955). For the other systems the methods of Brown and Fock (1956) were used.

TABLE I
ISOPROPANOL+BENZENE
Refractive index; composition data

x_1	$n_D^{25.00}$	x_1	$n_D^{25.00}$
0.0528	1.49150	0.4980	1.43899
0.1067	1.48511	0.5017	1.43853
0.2087	1.47317	0.5983	1.42681
0.3057	1.46182	0.7131	1.41256
0.3931	1.45149	0.8053	1.40083
0.4898	1.43997	0.9033	1.38805
0.4932	1.43952	0.9494	1.38189

The liquid-vapour equilibrium measurements for the system *isopropanol*+benzene were made by using the apparatus and methods of Brown and Smith (1955). The analysis was by refractive index measurements with a Hilger-Chance precision refractometer maintained at 25.00 ± 0.01 °C. The refractive index and composition data for this system are given in Table 1;

* Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

they were obtained from mixtures prepared by weighing. The method of Brown and Smith (1954) was employed to calculate the composition of the liquid and vapour samples.

III. COMPONENTS

The ethanol, benzene, and 2,2,4-trimethylpentane were purified by the methods described by Brown and Smith (loc. cit.) and Brown and Fock (loc. cit.). The *isopropanol* (Analar quality) was purified by distillation and was dried by azeotropic distillation with purified benzene in a 1.2 m column packed with 1.6 mm Dixon packing, operated at a reflux ratio of 50:1. The toluene was distilled using the same column and the centre fraction was scrubbed with concentrated sulphuric acid, washed, dried, and refractionated. The methylcyclohexane was purified in the same way as the toluene.

The density and refractive index values for the purified components are shown in Table 2.

TABLE 2
PHYSICAL PROPERTIES OF COMPONENTS

Component	$d_{4}^{25.00}$	$n_D^{25.00}$
Ethanol	0.78511	1.35928
<i>iso</i> Propanol	0.78089	1.37503
Benzene	0.87370	1.49799
Toluene	0.86224	1.49406
Methylcyclohexane	0.76515	—
2,2,4-Trimethylpentane	0.68778	1.38905

The vapour pressure of *isopropanol* was measured by using the equilibrium still. The vapour pressure data are shown in Table 3. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log P = A - \frac{B}{C + t}$$

where P is in standard mm Hg and t in °C. The values of the constants, the standard deviation σ of the fit, the calculated values of the boiling point at 760 mm Hg, and the vapour pressure at 45 °C are also given in Table 3.

TABLE 3
VAPOUR PRESSURE OF ISOPROPANOL

t (°C)	P (mm Hg)	Antoine Equation Constants
41.31	111.51	$A = 7.76677$ $B = 1371.59$ $C = 198.490$ $\sigma = 0.12$ mm Hg B.p./760 mm Hg (°C), 82.23 V.p. 45.00 °C (mm Hg), 136.05
44.99	135.87	
45.18	137.44	
49.09	168.41	
57.72	259.00	
64.93	363.11	
70.35	462.34	
75.10	566.93	
78.48	652.61	
82.17	758.13	
82.26	760.51	

IV. EXPERIMENTAL RESULTS

(a) *Heats of Mixing*

The results of the heat of mixing measurements for the systems ethanol+toluene at 35 °C, ethanol+methylcyclohexane at 35 °C, and *iso*-

TABLE 4
HEATS OF MIXING
Ethanol+toluene 35.00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0.122	859	0.676	631
0.217	983	0.681	612
0.379	998	0.691	586
0.603	738	0.873	264
0.605	740		

TABLE 5
HEATS OF MIXING
Ethanol+methylcyclohexane 35.00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0.129	574	0.712	478
0.247	685	0.719	515
0.426	695	0.719	506
0.657	553	0.723	470
0.665	529	0.888	276
0.670	541	0.892	257

TABLE 6
HEATS OF MIXING
*iso*Propanol+benzene 45.00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0.118	1163	0.495	1687
0.131	1213	0.499	1638
0.233	1552	0.571	1548
0.284	1637	0.581	1521
0.490	1655	0.816	866

propanol+benzene at 45 °C are given in Tables 4, 5, and 6 respectively; x_1 is the mole fraction of the alcohol and H^M is the heat of mixing in joules per mole (J/mol) of mixture

(b) *Liquid-Vapour Equilibrium Data*

The liquid-vapour equilibrium data for the system *isopropanol*+benzene at 45 °C are given in Table 7; x_1 and y_1 are the mole fractions of *isopropanol* in the liquid and vapour respectively, P is the total pressure in standard mm Hg and α is the relative volatility.

Graphs of the data in Table 7 show that *isopropanol*+benzene forms an azeotrope at 45.00 °C, having a mole fraction of 0.296 *isopropanol* at a total pressure of 273.4 mm Hg.

TABLE 7
EXPERIMENTAL DATA AND DERIVED FUNCTIONS
isoPropanol+benzene at 45.00 °C

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0.0472	0.1467	252.50	3.470	1108.3	6.0	58.0
0.0980	0.2066	264.13	2.397	889.8	22.8	107.8
0.2047	0.2663	272.06	1.410	601.6	71.8	180.3
0.2960	0.2953	273.40	0.9966	436.3	126.7	218.3
0.3862	0.3211	272.22	0.7517	317.8	187.4	237.8
0.4753	0.3463	269.49	0.5848	227.8	256.6	242.9
0.5504	0.3692	264.92	0.4781	164.5	321.2	235.0
0.6198	0.3951	259.35	0.4007	118.8	387.8	221.1
0.7096	0.4378	247.70	0.3187	69.0	483.5	189.4
0.8073	0.5107	227.14	0.2491	30.3	601.8	140.4
0.9120	0.6658	189.28	0.1922	6.8	744.1	71.7
0.9655	0.8252	159.80	0.1687	0.8	821.8	29.1

V. EXCESS FREE-ENERGY DATA

The values of the excess chemical potentials μ_1^E , μ_2^E and the excess free energy of mixing G_x^E for the system *isopropanol*+benzene were calculated from the data given in Table 7, using equations (1), (2), and (3):

$$\mu_1^E = RT \ln Py_1/P_1x_1 + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2 + \frac{1}{2}D_{11}\{(4y_1^3 - 3y_1^4)P^3 - P_1^3\}, \quad \dots\dots (1)$$

$$\mu_2^E = RT \ln Py_2/P_2x_2 + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2 - D_{11}\{y_1^4P^3\}, \quad \dots\dots (2)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \quad \dots\dots\dots (3)$$

where P_1 and P_2 are the vapour pressures of the pure components, V_1 and V_2 the liquid molar volumes, β_{11} , β_{22} , β_{12} , and D_{11} are coefficients in the equations of state for the pure and mixed vapours. δ_{12} is given by

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}.$$

The equation of state for the pure component vapours was taken as

$$V = RT/P + \beta_{jj} + D_{jj}P^2,$$

and that for the mixed vapour as

$$V_{12} = RT/P + \beta_{11}y_1^2 + 2\beta_{12}y_1y_2 + \beta_{22}y_2^2 + D_{11}y_1^4P^2.$$

The value of D_{22} for benzene was assumed to be zero and the values of the other coefficients were calculated from equations given by Kretschmer and Wiebe (1954) for *isopropanol* and by Allen, Everett, and Penney (1952) for benzene. The value of β_{12} was evaluated by the method given by Brown and Smith (1954).

The values of the coefficients at 45 °C were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2	D_{11}	D_{22}
-2.15	-1.23	-0.97	1.44	0.079	0.092	-1.195×10^{-5}	0

Units are l/mol except D_{11} , which is in l/mm² mole.

The values of the correction terms involving D_{11} in equations (1) and (2) were less than 1 cal/mol.

Values of the derived thermodynamic functions are given in Table 7 in calories per mole of mixture.

The excess free-energy data were fitted by the method of least squares to equation (4)

$$G_x^E = x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2]. \quad \dots\dots\dots (4)$$

The values of the constants in this equation and the standard deviation σ of the fit were found to be, in cal/mol,

$$a = 963.7, \quad b = -173.0, \quad c = 134.3, \quad \sigma = 1.7.$$

These values do not indicate separation into two liquid phases.

The excess free-energy data were shown to be thermodynamically consistent by comparing the areas above and below datum on a plot of $\mu_1^E - \mu_2^E$ against x_1 ; their ratio was 1.002.

The excess free energy of mixing for the systems containing 2,2,4-trimethylpentane, toluene, and methylcyclohexane was calculated from the experimental data of Kretschmer, Nowakovska, and Wiebe (1948) and Kretschmer and Wiebe (1949a, 1949b). The non-ideality of the vapours was allowed for by using the method of Brown and Smith (1954), values of β_{22} being calculated from the Berthelot equation. The values used were (l/mol)

2,2,4-Trimethylpentane 25 °C	..	-2.34
Toluene 35 °C	-1.75
Methylcyclohexane 35 °C	-1.90

The excess free-energy data for the system ethanol+benzene have been determined by Brown and Smith (1954).

VI. THERMODYNAMIC PROPERTIES

The excess free energy G_x^E , heat of mixing H_x^M , and excess entropy of mixing TS_x^E for the five alcohol systems were calculated at even mole fractions, at the temperature of measurement, from the data given in the earlier sections of the

TABLE 8
THERMODYNAMIC PROPERTIES
Ethanol + benzene 45 °C

x_1	G_x^E	H_x^M	TS_x^E
0.1	125	230	+105
0.2	202	294	+92
0.3	247	315	+68
0.4	267	312	+45
0.5	268	285	+17
0.6	250	241	-9
0.7	215	189	-26
0.8	160	132	-28
0.9	88	68	-20

TABLE 9
THERMODYNAMIC PROPERTIES
Ethanol + toluene 35 °C

x_1	G_x^E	H_x^M	TS_x^E
0.1	140	182	+42
0.2	213	231	+18
0.3	258	243	-15
0.4	286	235	-51
0.5	288	210	-78
0.6	267	178	-89
0.7	231	140	-91
0.8	172	97	-75
0.9	98	50	-48

TABLE 10
THERMODYNAMIC PROPERTIES
Ethanol + 2,2,4-trimethylpentane 25 °C

x_1	G_x^E	H_x^M	TS_x^E
0.1	158	123	-35
0.2	250	150	-100
0.3	304	162	-142
0.4	334	161	-173
0.5	340	152	-188
0.6	321	138	-183
0.7	284	119	-165
0.8	225	93	-132
0.9	136	57	-79

present paper. $T^{\circ}\text{K} = t^{\circ}\text{C} + 273.16$, $1 \text{ cal} = 4.1840 \text{ abs. joules}$. These data are given in cal/mol of mixture in Tables 8 to 12. For the systems containing toluene, methylcyclohexane, and 2,2,4-trimethylpentane Kretschmer, Nowakowska, and Wiebe (1948) and Kretschmer and Wiebe (1949a, 1949b) calculated

TABLE 11
THERMODYNAMIC PROPERTIES
Ethanol+methylcyclohexane 35 °C

x_1	G_x^E	H_x^M	TS_x^E
0.1	165	121	— 44
0.2	254	158	— 96
0.3	306	168	—138
0.4	334	167	—167
0.5	339	159	—180
0.6	320	143	—177
0.7	280	122	—158
0.8	217	94	—123
0.9	126	59	— 67

heats of mixing from the excess free-energy data at two temperatures. Their values are approximately 30 per cent. higher and more symmetrical in mole fraction than the directly measured values given above.

TABLE 12
THERMODYNAMIC PROPERTIES
isoPropanol+benzene 45 °C

x_1	G_x^E	H_x^M	TS_x^E
0.1	110	251	141
0.2	177	350	173
0.3	219	397	178
0.4	240	408	168
0.5	241	393	152
0.6	225	357	132
0.7	193	299	106
0.8	145	222	77
0.9	80	123	43

VII. DISCUSSION

The results given here, together with the results of Scatchard and Ticknor (1952) for methanol+benzene and those of Barker, Brown, and Smith (1953) for ethanol+carbon tetrachloride, enable some interesting comparisons to be made.

If we compare the thermodynamic properties of the ethanol systems we find that those having non-aromatic components are similar, while those with

aromatic components have more positive values of the excess entropy and heat of mixing. This indicates stronger interaction of alcohol molecules with aromatic than with non-aromatic molecules. This causes increased breaking of alcohol hydrogen bonds and this occurs at a higher concentration of alcohol in aromatic systems than in non-aromatic systems.

Comparison of the systems containing benzene with different alcohols shows that the heat and excess entropy of mixing become rapidly more positive as the hydrocarbon chain of the alcohol molecule becomes longer. More positive heats of mixing could be due either to a larger heat change on breaking an individual hydrogen bond or to the fact that more hydrogen bonds are broken in solutions of longer-chain alcohols. Increased heat of breaking individual hydrogen bonds would be expected to lead to more *negative* excess entropy of mixing. The second alternative, however, is consistent with the observed increase of both heat of mixing and excess entropy of mixing with alcohol chain-length. If more hydrogen bonds are broken at a given concentration in systems with longer-chain alcohols, this can only be because the entropy increase on breaking an individual hydrogen bond is larger in these systems. This is presumably associated with a larger gain in configurational freedom on breaking hydrogen bonds between longer-chain alcohol molecules. It is uncertain how far this increase continues as the size of the alcohol molecule increases, but the corresponding properties calculated from less reliable data listed in Appendix I for *n*-propanol+benzene and the four butanol+benzene systems suggest that the properties of the butanol systems are not very different from those of the isopropanol system.

VIII. ACKNOWLEDGMENTS

The authors wish to thank Mr. J. A. Barker and Mr. O. H. Rigby for their help with this work.

IX. REFERENCES

- ALLEN, P. W., EVERETT, D. H., and PENNEY, M. F. (1952).—*Proc. Roy. Soc. A* **212**: 149.
ALLEN, B. B., LINGO, S. P., and FELSING, W. A. (1939).—*J. Phys. Chem.* **43**: 425.
BARKER, J. A., BROWN, I., and SMITH, F. (1953).—*Disc. Faraday Soc.* **15**: 142.
BROWN, I., and FOCK, W. (1955).—*Aust. J. Chem.* **8**: 361.
BROWN, I., and FOCK, W. (1956).—*Aust. J. Chem.* **9**: 180.
BROWN, I., and SMITH, F. (1954).—*Aust. J. Chem.* **7**: 264.
BROWN, I., and SMITH, F. (1955).—*Aust. J. Chem.* **8**: 501.
KRETSCHMER, C. B., NOWAKOWSKA, J., and WIEBE, R. (1948).—*J. Amer. Chem. Soc.* **70**: 1785.
KRETSCHMER, C. B., and WIEBE, R. (1949a).—*J. Amer. Chem. Soc.* **71**: 1793.
KRETSCHMER, C. B., and WIEBE, R. (1949b).—*J. Amer. Chem. Soc.* **71**: 3176.
KRETSCHMER, C. B., and WIEBE, R. (1954).—*J. Amer. Chem. Soc.* **76**: 2579.
LEE, S. C. (1931).—*J. Phys. Chem.* **35**: 3558.
OLSEN, A. L., and WASHBURN, E. R. (1937).—*J. Phys. Chem.* **41**: 457.
PAHLKE, H. (1935).—"Landolt-Börnstein Tabellen." (Springer: Berlin.)
PERRAKIS, N. (1925).—*J. Chim. Phys.* **22**: 296.
SCATCHARD, G., and TICKNOR, L. B. (1952).—*J. Amer. Chem. Soc.* **74**: 3724.
WILLINGHAM, C. B., TAYLOR, W. J., PIGNOCCO, J. M., and ROSSINI, F. D. (1945).—*J. Res. Nat. Bur. Stand.* **35**: 219.

APPENDIX I

<i>n</i> -Propanol + benzene 40 °C	(Lee 1931)	
<i>iso</i> Propanol + benzene 25 °C	(Olsen and Washburn 1937)	
<i>n</i> -Butanol + benzene 25 °C	} (Allen, Lingo, and Felsing 1939)	
<i>iso</i> Butanol + benzene 25 °C		
<i>sec.</i> -Butanol + benzene 25 °C		
<i>tert.</i> -Butanol + benzene 25 °C		
<i>n</i> -Propanol + benzene 20 °C	} (Pahlke 1935)	
<i>iso</i> Propanol + benzene 20 °C		
<i>tert.</i> -Butanol + benzene 20 °C		
<i>n</i> -Butanol + benzene 20 °C		(Perrakis 1925 ; Pahlke 1935).

THE CONDENSATION OF ACETYLENES WITH DEOXYANISOLIN

By J. CYMERMAN-CRAIG,* D. MARTIN,* M. MOYLE,* and
P. C. WAILES*

[Manuscript received October 27, 1955]

Summary

Although deoxyanisoin underwent fission on attempted reaction with sodium or lithium acetylide in liquid ammonia, it condensed normally with 1-hexyne and propyne via the Grignard reagent, the intermediate acetylenic carbinols dehydrating on distillation. The reaction of acetylenedimagnesium bromide and deoxyanisoin at room temperature afforded the stable 1,2-di-(*p*-methoxyphenyl)but-3-yn-2-ol, whereas the same reagents under more vigorous conditions resulted in cyclization to 2-methoxy-6-*p*-methoxyphenylnaphthalene, synthesized from anisil or deoxyanisoin by a Reformatsky reaction via the tetralone.

I. INTRODUCTION

Apart from the description by Nazarov and Kotlyarevski (1950) of the condensation with vinylacetylene, the reaction of deoxyanisoin with acetylenes has not been studied. The expected products of such condensations are of interest for their possible oestrogenic properties and the reactions of deoxyanisoin with acetylene and certain substituted acetylenes are reported in the present paper.

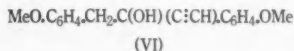
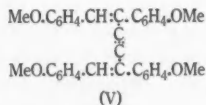
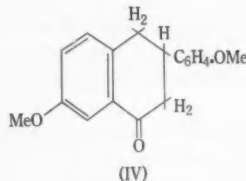
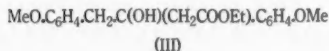
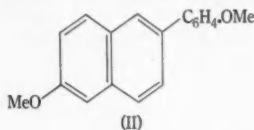
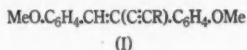
Attempted condensation of deoxyanisoin with propargyl alcohol failed under all conditions tried. However, deoxyanisoin condensed normally with 1-hexynylmagnesium bromide and the main product (71 per cent.), when isolated by distillation so that the carbinol first formed was dehydrated, was 1,2-di-(*p*-methoxyphenyl)oct-1-en-3-yne (I; R=*n*-Bu). Dehydration would be expected to give the *trans*-form of I. In agreement, a freshly prepared solution of I (R=*n*-Bu) showed light absorption at 2200 and 3300 Å. After exposure to sunlight for a few hr, or on irradiation with an ultraviolet source for 20 min, the maxima had shifted to 2220 and 3080 Å, suggestive of a rearrangement of a *trans*- to a *cis*-structure. The constitution of I (R=*n*-Bu) follows from its ready absorption of 3 mols of hydrogen to give 1,2-di-(*p*-methoxyphenyl)octane.

Similarly, condensation of deoxyanisoin with propynylmagnesium bromide gave on distillation 1,2-di-(*p*-methoxyphenyl)pent-1-en-3-yne (I; R=Me), showing light absorption behaviour identical with the butyl analogue. Both isomers appeared to be relatively stable, as the irradiated solution did not undergo further change on standing in the dark. The structure of I (R=Me) was proved rigidly by hydrogenation when 3 mols of hydrogen were absorbed to give 1,2-di-(*p*-methoxyphenyl)pentane. This was synthesized by condensation of deoxyanisoin with *n*-propylmagnesium iodide, followed by catalytic reduction of the dehydrated carbinol.

* Department of Organic Chemistry, University of Sydney.

The synthesis of 1,2-di-(*p*-methoxyphenyl)but-1-en-3-yne (I; R=H) was attempted by condensation of deoxyanisoin with sodium acetylide in liquid ammonia. Molecular fission occurred giving anisic acid, anisamide, and 3-*p*-methoxyphenylprop-1-yn-3-ol, characterized as the α -naphthylurethane. The use of lithium acetylide (Campbell and Campbell 1940) which has often been successful where the sodium derivative had failed (Oroshnik and Mebane 1949; Elsner and Paul 1951) gave only anisic acid and anisamide, while employment of acetaldehyde di-*n*-butyl acetal as solvent for the reaction of deoxyanisoin with acetylene in the presence of potassium hydroxide (Bergmann, Sulzbacher, and Herman 1953) gave a 95 per cent. recovery of deoxyanisoin.

Acetylenedimagnesium bromide is known to exist in equilibrium with some of the monomagnesium derivative; thus Gvertsiteli (1948) obtained 1,2-diphenylbut-3-yn-1,2-diol from benzoin and acetylenedimagnesium bromide. Condensation of deoxyanisoin with acetylenedimagnesium bromide during 90 hr at



room temperature gave the sparingly-soluble 1,2,5,6-tetra-(*p*-methoxyphenyl)hexa-1,5-dien-3-yne (V). Its maleic anhydride adduct polymerized on attempted purification, as did the tetramethyl ester obtained using diazomethane on the corresponding acid. The instability of the adduct is undoubtedly due to its 1,4-diphenylbutadiene structure.

After removal of the dienyne, chromatography of the non-ketonic portion gave a low yield of 1,2-di-(*p*-methoxyphenyl)but-3-yn-2-ol (VI), m.p. 95 °C. It showed infra-red absorption ("Nujol" mull) at 3460 cm^{-1} (OH) and 3250 cm^{-1} ($\equiv\text{CH}$). Surprisingly, it distilled without dehydration in a high vacuum, giving a second crystalline form, m.p. 87 °C, of the butynol (VI). Its infra-red spectrum showed maxima at 3480 and 3250 cm^{-1} .

Recently, Hofstetter and Wilder Smith (1953*a*, 1953*b*) reported inability to dehydrate the closely related 3,4-di-(*p*-methoxyphenyl)hex-1-yn-3-ol, which distilled unchanged at 195 °C/0.6 mm.

When the reaction between acetylenedimagnesium bromide and deoxyanisoin was carried out by refluxing for 60 hr, distillation gave a product, m.p.

192.5 °C, analysing for the desired I (R=H). However, it gave a negative test with Tollens's reagent and its absorption spectrum differed sharply from that of the homologous I (R=alkyl), resembling instead that of 2-phenylnaphthalene. Repetition of the Grignard reaction with only intermittent heating for 70 hr gave a product, m.p. 183–184 °C, showing light absorption identical with that of the compound, m.p. 192.5 °C, to which it was converted by prolonged boiling with ethanol. It was possible that cyclization of the expected product I (R=H) had occurred, giving 2-methoxy-6-*p*-methoxyphenylnaphthalene (II), and the synthesis of this was undertaken.

Reformatsky reaction of deoxyanisoin followed by simultaneous dehydration, hydrolysis, and reduction of the resulting ethyl 2-hydroxy-2,3-di-(*p*-methoxyphenyl)butyrate (III) gave 2,3-di-(*p*-methoxyphenyl)butyric acid directly. Slow addition of 1 mol of ethyl bromoacetate to zinc and anisil gave ethyl 2,3-di-(*p*-methoxyphenyl)-2-hydroxy-3-ketobutyrate, which was also converted without isolation, to 2,3-di-(*p*-methoxyphenyl)butyric acid. Dehydration by polyphosphoric acid (Koo 1953) gave 85 per cent. 4-keto-6-methoxy-2-*p*-methoxyphenyl-1,2,3,4-tetrahydronaphthalene (IV). Use of the inverse Friedel-Crafts cyclization (Johnson and Glenn 1949) resulted in 24 per cent. of this tetralone, with considerable tar formation probably due to partial demethylation caused by the aluminium chloride reagent. Lithium aluminium hydride reduction of the tetralone gave the tetralol in 90 per cent. yield, readily dehydrated by phosphorus pentoxide (Campbell and Kidd 1954). Attempted direct conversion of the tetralol to the naphthalene by means of thionyl chloride gave only tars, but dehydrogenation by means of chloranil afforded 2-methoxy-6-*p*-methoxyphenylnaphthalene (II), identical (m.p. 193–194 °C) with the product obtained from acetylenedimagnesium bromide. Lack of material prevented investigation of the mechanism of formation of this naphthalene from acetylenedimagnesium bromide and deoxyanisoin.

Hydrolysis of 2-methoxy-6-*p*-methoxyphenylnaphthalene gave 6-*p*-hydroxyphenyl-2-naphthol, and the same product was obtained on attempted hydrolysis of 6-methoxy-2-*p*-methoxyphenyl-1,2-dihydronaphthalene.

The compounds I (R=*n*-Bu; R=Me), V, II, and 6-*p*-hydroxyphenyl-2-naphthol were tested for oestrogenic activity in mice by Dr. J. D. Biggers and Dr. P. Claringbold, Department of Veterinary Physiology, University of Sydney, using the Allen-Doisy technique, and were found to be inactive at a dose of 1 mg per mouse.

II. EXPERIMENTAL

All known products were identified by melting point and mixed melting point.

(a) *1,2-Di-(p-methoxyphenyl)oct-1-en-3-yne*.—1-Hexyne (12.3 g; 0.15 mol) was refluxed with ethylmagnesium bromide (from 2.43 g of Mg) for 3 hr. After addition of finely powdered deoxyanisoin (12.8 g; 0.05 mol) and ether (100 ml), heating was continued for a further 2 hr and the clear solution allowed to stand overnight. The complex was hydrolysed with ammonium chloride solution and sulphuric acid (2N) in the usual manner. Acidification of the sodium bicarbonate washings of the ethereal extracts gave anisic acid (0.5 g, 6.5% yield).

Removal of solvent from the dried (Na₂SO₄) ethereal extracts gave a residue (16.8 g) which lost water at 100 °C/30 mm. Distillation gave 2 fractions: (i) b.p. c. 60 °C/0.05 mm, n_D^{18} 1.4898,

dodeca-5,7-di-yne (0.7 g, 6% yield) (Found: C, 88.6; H, 11.5%. Calc. for $C_{12}H_{18}$: C, 88.8; H, 11.2%). Armitage, Jones, and Whiting (1951) give n_D^{16} 1.4920. (ii) b.p. c. 206 °C/0.08 mm, $n_D^{20.5}$ 1.6230, which solidified and crystallized from methanol as colourless rhombic plates (12 g, 71% yield) of 1,2-di-(p-methoxyphenyl)oct-1-en-3-yne, m.p. 57 °C (Found: C, 82.5; H, 7.5%. Calc. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.5%).

(b) 1,2-Di-(p-methoxyphenyl)octane.—The preceding octenyne, hydrogenated in methanol solution with platonic oxide catalyst, absorbed 3.0 mol of H per mol of substance. Working up gave 1,2-di-(p-methoxyphenyl)octane as a viscous oil, b.p. 160 °C/0.05 mm, n_D^{20} 1.5420 (Found: C, 80.6; H, 9.1%. Calc. for $C_{22}H_{26}O_2$: C, 80.9; H, 9.2%).

(c) 1,2-Di-(p-methoxyphenyl)pent-1-en-3-yne.—1-Propynylmagnesium bromide was prepared by Heisig and Davis's (1935) method from propyne and ethylmagnesium bromide (from 2.43 g of Mg) and finely powdered deoxyanisoin (12.8 g; 0.05 mol) added. Refluxing was continued for 8 hr and the mixture worked up as described. No acidic fraction was obtained. The neutral fraction (13.1 g) was treated with Girard P reagent (17 g) by Girard and Sandulesco's (1936) method, except the mixture was extracted with ether and benzene immediately after pouring into potassium carbonate solution. The ketonic portion gave deoxyanisoin (4.55 g). The non-ketonic fraction crystallized from ethanol as colourless needles (7.3 g, 49.5% yield) of 1,2-di-(p-methoxyphenyl)pent-1-en-3-yne, m.p. 126 °C (Found: C, 82.0; H, 6.5%. Calc. for $C_{18}H_{18}O_2$: C, 82.0; H, 6.5%). The substance instantly decolourized a solution of bromine in carbon tetrachloride.

(d) 1,2-Di-(p-methoxyphenyl)pentane.—(i) The above pentenyne, hydrogenated in methyl acetate solution in presence of platonic oxide catalyst, absorbed 3.0 mol of H per mol. Working up gave 1,2-di-(p-methoxyphenyl)pentane as a viscous oil, b.p. 160 °C/0.4 mm, n_D^{21} 1.5540, solidifying to white plates, m.p. 31 °C (Found: C, 80.6; H, 8.5%. Calc. for $C_{19}H_{24}O_2$: C, 80.2; H, 8.5%).

(ii) A solution of *n*-propylmagnesium iodide (from 1 g of Mg) was treated gradually with deoxyanisoin (5.1 g; 0.02 mol) in benzene (70 ml) with vigorous stirring, and the solution was refluxed and stirred for a further 9 hr. Working up gave a solid (4.8 g) which showed no ketonic reactions. Extraction with light petroleum (b.p. 40–60 °C) and washing the insoluble residue with ethanol left 4,4'-dimethoxystilbene (1.3 g, 27% yield) crystallizing from ethyl acetate as white plates, m.p. and mixed m.p. 210 °C.

Distillation of the light petroleum solution caused elimination of water and 1,2-di-(p-methoxyphenyl)pent-1-ene distilled as a pale yellow liquid, b.p. 175–178 °C/1 mm, $n_D^{24.5}$ 1.5914 (Found: C, 80.8; H, 7.9%. Calc. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.8%). It instantly decolourized a solution of bromine in carbon tetrachloride.

(iii) The above pentene, hydrogenated in a mixture of methanol and methyl acetate in presence of platonic oxide, absorbed 1 mol of H per mol. Working up gave 1,2-di-(p-methoxyphenyl)pentane, b.p. 160–162 °C/0.4 mm, solidifying to white plates, m.p. 30 °C, undepressed on admixture with the material prepared in Section II (d) (i).

(e) Condensation of Deoxyanisoin with Sodium Acetylide.—Deoxyanisoin (25.6 g; 0.1 mol) and ether (200 ml) were added during 0.5 hr to sodium acetylide (from 7.5 g of Na; 0.35 mol) in liquid ammonia (800 ml). The brownish yellow mixture was stirred vigorously for 7.5 hr and worked up as in Section II (a), except a final extraction with benzene was necessary to dissolve an ether-insoluble product.

An acidic fraction of anisic acid (2.3 g, 15% yield) and a basic fraction of anisamide (0.78 g, 5% yield) were obtained.

The neutral fraction gave deoxyanisoin (13.1 g) on distillation of the benzene extracts, and the neutral ethereal extracts left a residue (10.3 g) which was treated with Girard P reagent, giving a ketonic portion of deoxyanisoin (7 g) and a non-ketonic oil, which on distillation gave 3-*p*-methoxyphenylprop-1-yn-3-ol (1 g, 6% yield) as a colourless liquid, b.p. c. 76–77 °C/0.05 mm, $n_D^{22.5}$ 1.5376 (Found: C, 74.1; H, 6.6%. Calc. for $C_{10}H_{10}O_2$: C, 74.0; H, 6.2%). It gave

an immediate precipitate with Tollens's reagent. Rutan and May (1947) give b.p. $123.5^{\circ}\text{C}/0.5\text{ mm.}$ The α -naphthylurethane formed at room temperature after 7 days, and crystallized from light petroleum (b.p. $100\text{--}120^{\circ}\text{C}$) as prisms, m.p. 135.5°C (Found: C, 76.1; H, 5.4; N, 4.5%. Calc. for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$: C, 76.1; H, 5.2; N, 4.2%). The residue from the distillation was a light brown solid (1.7 g), m.p. $145\text{--}150^{\circ}\text{C}$.

(f) *Condensation of Deoxyanisolin with Lithium Acetylide.*—Repetition of the previous experiment, but using lithium (3.5 g; 0.5 mol) instead of sodium, gave unchanged deoxyanisolin as an ether-insoluble solid (14 g). The acidic fraction was anisic acid (1.55 g) and the basic fraction was anisamide (0.1 g).

The neutral ethereal extracts left a residue (12.35 g) which after treatment with Girard P reagent gave as ketonic fraction a further 5.6 g of deoxyanisolin.

(g) *Reaction of Deoxyanisolin with Acetylenedimagnesium Bromide.*—(i) Deoxyanisolin (12.8 g; 0.05 mol) was added to vigorously stirred acetylenedimagnesium bromide (from 24 g of Mg; 1 mol) (Heilbron, Jones, and Raphael 1943) in ether (1 l.) and the mixture refluxed for 60 hr, a stream of acetylene being passed through the mixture.

Working up in the usual manner gave on distillation under reduced pressure a yellow oil, b.p. c. $190\text{--}200^{\circ}\text{C}/0.06\text{ mm.}$, which solidified and crystallized from benzene-light petroleum (b.p. $60\text{--}90^{\circ}\text{C}$) as white plates, m.p. 192.5°C , of 2-methoxy-6-(*p*-methoxyphenyl)naphthalene (0.6 g, 4.5% yield) (Found: C, 82.0; H, 6.4%. Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.8; H, 6.1%). It gave a negative test with Tollens's reagent. A mixed m.p. with the authentic substance prepared in Section II (m) was undepressed.

The distillation residue on extraction with light petroleum (b.p. $100\text{--}120^{\circ}\text{C}$) gave yellow prisms, m.p. $224\text{--}226.5^{\circ}\text{C}$ (0.5 g, 4% yield), undepressed on admixture with 1,2,5,6-tetra-(*p*-methoxyphenyl)hexa-1,5-dien-3-yne, m.p. 228°C , prepared as follows.

(ii) The above experiment was repeated, adding deoxyanisolin (12.8 g; 0.05 mol) in benzene (150 ml) to acetylenedimagnesium bromide (from 12 g of Mg; 0.5 mol) followed by continued passage of acetylene with vigorous stirring for 70 hr, the mixture being brought to $50\text{--}60^{\circ}\text{C}$ only once every 8 hr.

During working up, a solid separating at the interface was collected, boiled with ethanol, and the insoluble residue (1.15 g, 9.5% yield) crystallized from xylene (Soxhlet) as yellow needles, m.p. 228°C , of 1,2,5,6-tetra-(*p*-methoxyphenyl)hexa-1,5-dien-3-yne (Found: C, 81.3; H, 6.1; O, 12.3%; mol. wt. (Rast), 580, 490. Calc. for $\text{C}_{24}\text{H}_{20}\text{O}_4$: C, 81.3; H, 6.0; O, 12.7%; mol. wt., 502). The substance was almost insoluble in hot ethanol and only slightly soluble in boiling toluene and xylene.

Removal of solvent from the ether and benzene extracts gave an orange residue which on boiling with ethanol left a further 0.15 g (1% yield) of the dienyne, m.p. and mixed m.p. 228°C .

The residue from the evaporation of the combined ethanolic filtrates was treated with Girard P reagent. The ketonic fraction was deoxyanisolin (1 g). Distillation of the non-ketonic fraction afforded an oil, b.p. c. $180\text{--}190^{\circ}\text{C}/0.04\text{ mm.}$ (0.4 g, 3% yield), which solidified to white plates, m.p. $183\text{--}184^{\circ}\text{C}$ (Found: mol. wt. (Rast), 226. Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_2$: mol. wt., 264), which on boiling with ethanol changed to m.p. 192.5°C identical with that obtained in Section II (g) (i).

(iii) The above experiment was repeated, adding deoxyanisolin (51.2 g) in benzene (600 ml) to acetylenedimagnesium bromide (from 9.6 g of Mg), and stirring the solution for a further 90 hr with continued passage of acetylene; the volume was maintained at 800 ml by addition of benzene as required.

Working up in the usual manner left a residue which was treated with Girard P reagent (35 g). The reaction mixture before pouring into potassium carbonate solution was filtered to remove yellow crystals of 1,2,5,6-tetra-(*p*-methoxyphenyl)hexa-1,5-dien-3-yne (4.2 g, 8.5% yield), m.p. and mixed m.p. 224°C . The ketonic portion gave deoxyanisolin (19.5 g), and a further 1 g (2% yield) of the ethanol-insoluble dienyne, m.p. and mixed m.p. 224°C .

The non-ketonic fraction, chromatographed on alumina using light petroleum (b.p. $60\text{--}90^{\circ}\text{C}$) containing an increasing percentage of benzene, gave a white solid (0.7 g, 1.5% yield) crystallizing

from hexane as prisms, m.p. 95 °C, of 1,2-di-(*p*-methoxyphenyl)but-3-yn-2-ol (Found: C, 76.7; H, 6.6%. Calc. for $C_{18}H_{16}O_3$: C, 76.6; H, 6.4%). It gave an immediate white precipitate with Tollens's reagent. On distillation it gave a colourless oil, b.p. c. 150 °C/0.001 mm, solidifying to white prisms, m.p. 87 °C, of the acetylenic alcohol (Found: C, 76.2; H, 6.6%). This also gave an immediate white precipitate with Tollens's reagent, and a mixed m.p. with the form m.p. 95 °C, showed m.p. 87–95 °C.

(h) *Ethyl 2-Hydroxy-2,3-di-(p-methoxyphenyl)butyrate*.—A mixture of ethyl bromoacetate (25.05 g; 1 mol) and deoxyanisoin (38.4 g; 1 mol) in benzene (400 ml) was added with stirring and refluxing to zinc filings (9.55 g; 1 mol) and benzene (100 ml) over 2 hr and the mixture stirred and refluxed for a further 2 hr.

Working up gave a viscous oil from which ether (300 ml) precipitated deoxyanisoin (3.6 g, 9.5% recovery), m.p. and mixed m.p. 110–111 °C. The ethereal solution was freed from solvent and from excess of ethyl bromoacetate at 100 °C/2 mm and the remainder (which still gave a positive ketonic reaction) treated with Girard P reagent. The ketonic fraction was deoxyanisoin (3.4 g), while the non-ketonic portion was *ethyl 2-hydroxy-2,3-di-(p-methoxyphenyl)butyrate* (36 g, 70% yield) crystallizing from methanol as white needles, m.p. 51–52 °C (Found: C, 69.8; H, 7.0%. Calc. for $C_{26}H_{24}O_4$: C, 69.7; H, 7.0%).

(i) *2,3-Di-(p-methoxyphenyl)butyric Acid*.—(i) The above 2-hydroxy ester (5 g) was refluxed with amalgamated zinc (15 g) in hydrochloric acid (45 ml; 10N) for 12 hr. The cold reaction mixture was extracted with benzene, and the benzene layers extracted with sodium hydroxide solution. Acidification of the alkaline solution gave *2,3-di-(p-methoxyphenyl)butyric acid* (1 g, 24% yield) crystallizing from ethanol as white microcrystals, m.p. 166–168 °C. Cook and Lawson (1933) give m.p. 167–168 °C. A second reduction of the neutral fraction gave no further acid. The yield was unaltered by extending the reaction period to 18 hr.

(ii) Ethyl bromoacetate (21 g) in benzene (50 ml) was added with stirring over 1.5 hr to a gently refluxing mixture of zinc filings (8.13 g) and anisil (33.75 g) in benzene (200 ml). The reaction mixture was refluxed with stirring for a further 4.5 hr. Working up and addition of ether (500 ml) to the residue from the benzene extracts gave unchanged anisil (10.8 g, 32% recovery). The ethereal solution gave a viscous oil, which was refluxed with amalgamated zinc (75 g) in hydrochloric acid (250 ml; 10N) for 16 hr, more amalgamated zinc (25 g) and hydrochloric acid (100 ml) then added, and the mixture refluxed a further 10 hr.

Working up as before gave the acid (12.5 g, 50% yield), m.p. 162–165 °C, identical with the material prepared in Section II (i) (i). The neutral fraction from the reduction afforded 1,2-di-(*p*-methoxyphenyl)ethane (2.6 g, 12.5% yield) as white needles from ethanol, m.p. and mixed m.p. 126–127 °C.

(j) *4-Keto-6-methoxy-2-p-methoxyphenyl-1,2,3,4-tetrahydronaphthalene*.—(i) On addition of 2,3-di-(*p*-methoxyphenyl)butyric acid (20 g) to polyphosphoric acid (from 85 g of phosphorus pentoxide and 85 ml of phosphoric acid), the mixture became pale brown. After stirring on the steam-bath for 2.5 hr the colour darkened to deep brown. The mixture was poured into ice-water (500 ml) and extracted with benzene. Removal of solvent from the washed (sodium hydroxide solution and water) extracts gave the *tetralone* (15.6 g, 83% yield) crystallizing from ethanol as white plates, m.p. 138–138.5 °C (Found: C, 76.5; H, 6.4%. Calc. for $C_{18}H_{14}O_2$: C, 76.5; H, 6.4%). The *2,4-dinitrophenylhydrazones* crystallized from acetic acid as red needles, m.p. 270 °C (decomp.) (Found: C, 61.8; H, 5.1%. Calc. for $C_{24}H_{22}O_6N_4$: C, 62.3; H, 4.8%).

(ii) Addition of thionyl chloride (4.8 g; 0.04 mol) to 2,3-di-(*p*-methoxyphenyl)butyric acid (60 g; 0.02 mol) caused the mixture to turn black. After heating on the water-bath for 10 min, thionyl chloride was removed by co-distillation with benzene (30 ml) *in vacuo* (20 mm). The residue was treated with powdered aluminium chloride (3.6 g; 0.025 mol) in benzene (75 ml) and the mixture heated on the water-bath until evolution of hydrogen chloride ceased. The cooled mixture was treated with ice (15 g), hydrochloric acid (6 ml; 10N), and ether (750 ml). The acid and alkali-washed, and dried (Na_2SO_4) ethereal extracts gave the *tetralone* (1.25 g, 23% yield) as a pale yellow viscous oil, b.p. 180–190 °C/0.001 mm, solidifying to white plates, m.p. and mixed m.p. 135–137 °C.

TABLE 1
ULTRAVIOLET LIGHT ABSORPTION IN 95 PER CENT. ETHANOL

Compound	λ_{\max} .	ϵ_{\max} .	λ_{\min} .	ϵ_{\min} .
3-(<i>p</i> -Methoxyphenyl)prop-1-yn-3-ol	2290 2740	11,400 3,000	2440	2200
1,2-Di-(<i>p</i> -methoxyphenyl)pent-1-en-3-yne ..	2190 2350* 3300	19,000 14,000 29,000	2620	4000
1,2-Di-(<i>p</i> -methoxyphenyl)pent-1-en-3-yne (after irradiation)	2220 2350* 3070	16,500 15,500 20,000	2620	7000
1,2-Di-(<i>p</i> -methoxyphenyl)oct-1-en-3-yne ..	2220 2425* 3300	20,000 12,800 28,000	2620	5000
1,2-Di-(<i>p</i> -methoxyphenyl)oct-1-en-3-yne (after irradiation)	2220 2400* 3080	16,500 16,000 19,000	2620	7500
Dodeca-5,7-diyne	2260 2400 2540* 2660 2730 2800	1,000 900 600 300 300 280		
1,2,5,6-Tetra-(<i>p</i> -methoxyphenyl)hexa-1,5-dien-3-yne†	2770 3260 3680	23,200 28,500 24,900		
1,2-Di-(<i>p</i> -methoxyphenyl)but-3-yn-2-ol (m.p. 95 °C)	2270 2750	18,600 3,200	2450	1500
1,2-Di-(<i>p</i> -methoxyphenyl)but-3-yn-2-ol (m.p. 87 °C)	2270 2750	17,100 8,000	2450	1800
2-Phenylnaphthalene‡	2130 2500 2850	28,200 50,000 11,200		
2-Methoxy-6-(<i>p</i> -methoxyphenyl)naphthalene (from acetylene reaction)	2210 2560 2950	33,000 39,500 21,000		
2-Methoxy-6-(<i>p</i> -methoxyphenyl)naphthalene (synthetic)	2220 2550 2950	32,500 41,000 21,000		
<i>trans</i> -4,4'-Dimethoxystilbene	2300 3000-3070 3250	12,600 24,000 22,100	2550	3700

* Inflexion. † In chloroform. ‡ Friedel and Orchin (1951).

(k) *4-Hydroxy-6-methoxy-2-p-methoxyphenyl-1,2,3,4-tetrahydronaphthalene*. — The preceding tetralone (14.5 g) was placed in the thimble of a Soxhlet extractor and refluxed with a mixture of lithium aluminium hydride (3 g; 1.5 mol) and ether (1500 ml). Dissolution of the tetralone required 4 hr, and the mixture was refluxed for a further 15 hr. Working up by addition of ice-water and sulphuric acid (2N) gave the *tetralol* (13.1 g, 90% yield) crystallizing from benzene-light petroleum (b.p. 60–90 °C) as white microcrystals, m.p. 114–115 °C (Found: C, 75.8; H, 7.1%. Calc. for $C_{18}H_{20}O_3$: C, 76.0; H, 7.1%).

(l) *6-Methoxy-2-p-methoxyphenyl-1,2-dihydronaphthalene*. — The above *tetralol* (3.15 g; 0.011 mol) was shaken with phosphorus pentoxide (3.2 g; 0.022 mol) in benzene (75 ml) for 5 hr. Water (30 ml) and ether (400 ml) were added and the washed (sodium carbonate solution and water) and dried (Na_2SO_4) extracts afforded the *dihydronaphthalene* (2.5 g, 85% yield) crystallizing from methanol as white needles, m.p. 93–94 °C (Found: C, 80.8; H, 6.8%. Calc. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8%).

(m) *2-Methoxy-6-p-methoxyphenylnaphthalene*. — The preceding *dihydronaphthalene* (1.2 g; 0.045 mol) was heated under reflux at 150 °C for 15 hr with chloranil (1.27 g; 0.005 mol) and sulphur-free xylene (15 ml). On cooling, the pale brown solid, which separated, was dissolved in benzene, and the benzene solution washed with potassium hydroxide solution (10%) until colourless, and finally with water. Removal of solvent *in vacuo* gave *2-methoxy-6-p-methoxyphenylnaphthalene* (0.66 g, 55% yield) crystallizing from benzene-light petroleum (b.p. 60–90 °C) as white plates, m.p. 193–194 °C (Found: C, 81.7; H, 6.1%. Calc. for $C_{18}H_{18}O_2$: C, 81.8; H, 6.1%).

(n) *6-p-Hydroxyphenyl-2-naphthol*. — A mixture of *2-methoxy-6-p-methoxyphenylnaphthalene* (0.7 g), ethanol (4.5 ml), and powdered potassium hydroxide (2 g) was heated in an autoclave for 24 hr at 200 °C. Water (50 ml) was added to the cold reaction mixture and the solution filtered hot. The filtrate was acidified at 0 °C with sulphuric acid (20%) and extracted with ether. The dried (Na_2SO_4) ethereal extracts gave *6-p-hydroxyphenyl-2-naphthol* (0.255 g, 42% yield) crystallizing from chlorobenzene as white needles, m.p. 258–262 °C, sintering at 250 °C, and rapidly darkening on repeated crystallization (Found: C, 80.7; H, 5.3%. Calc. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1%).

Reaction with acetic anhydride in pyridine at 100 °C gave *2-acetoxy-6-p-acetoxyphenylnaphthalene* crystallizing from methanol as white prisms, m.p. 176–177 °C (Found: C, 74.6; H, 5.2%. Calc. for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0%).

(o) *Attempted Hydrolysis of 6-Methoxy-2-p-methoxyphenyl-1,2-dihydronaphthalene*. — The *dihydronaphthalene* (1.33 g) in ether (20 ml) was added to methylmagnesium iodide (from 0.6 g of Mg) in ether (20 ml), solvents removed at 100 °C, and the residue slowly heated in an oil-bath to 170 °C until the evolution of gas had ceased. The cold residue was dissolved in ether and extracted with sodium hydroxide solution (5%). Acidification of the cold alkaline extracts gave an impure phenolic product, which on acetylation afforded *2-acetoxy-6-p-acetoxyphenylnaphthalene*, m.p. and mixed m.p. 175–177 °C.

Light Absorption. — Ultraviolet spectra were measured in 95% ethanol solution using a Unicam S.P. 500 spectrophotometer and are recorded in Table 1.

III. ACKNOWLEDGMENTS

Thanks are due to Dr. J. D. Biggers and Dr. P. Claringbold for carrying out the tests for oestrogenic activity.

IV. REFERENCES

- ARMITAGE, J. B., JONES, E. R. H., and WHITING, M. C. (1951).—*J. Chem. Soc.* **1951**: 44.
 BERGMANN, E. D., SULZBACHER, M., and HERMAN, D. F. (1953).—*J. Appl. Chem.* **3**: 39.
 CAMPBELL, K. N., and CAMPBELL, B. K. (1940).—*Proc. Indiana Acad. Sci.* **50**: 123.
 CAMPBELL, N., and KIDD, D. (1954).—*J. Chem. Soc.* **1954**: 2154.
 COOK, J. W., and LAWSON, W. (1933).—*J. Chem. Soc.* **1933**: 827.

- ELSNER, B. B., and PAUL, P. F. M. (1951).—*J. Chem. Soc.* **1951**: 893.
- FRIEDEL, R. A., and ORCHIN, M. (1951).—"Ultraviolet Spectra of Aromatic Compounds." (J. Wiley & Sons: New York.)
- GVERTSITEI, I. M. (1948).—*J. Gen. Chem. U.S.S.R.* **18**: 1187.
- HEILBRON, I. M., JONES, E. R. H., and RAPHAEL, R. A. (1943).—*J. Chem. Soc.* **1943**: 268.
- HEISIG, G. B., and DAVIS, H. M. (1935).—*J. Amer. Chem. Soc.* **57**: 339.
- HOFSTETTER, E., and WILDER SMITH, A. E. (1953a).—*Helv. Chim. Acta* **36**: 1706.
- HOFSTETTER, E., and WILDER SMITH, A. E. (1953b).—*Helv. Chim. Acta* **36**: 1949.
- JOHNSON, W. S., and GLENN, H. J. (1949).—*J. Amer. Chem. Soc.* **71**: 1092.
- KOO, J. (1953).—*J. Amer. Chem. Soc.* **75**: 1891.
- NAZAROV, I. N., and KOTLYAREVSKI, I. L. (1950).—*J. Gen. Chem. U.S.S.R.* **20**: 1431.
- OROSHNIK, W., and MEBANE, A. D. (1949).—*J. Amer. Chem. Soc.* **71**: 2062.
- RUTAN, P., and MAY, C. E. (1947).—*J. Amer. Chem. Soc.* **69**: 2017

THE S_N MECHANISM IN AROMATIC COMPOUNDS

XX. THE NUCLEOPHILICITY OF PHENOXIDES

By G. D. LEAHY,* M. LIVERIS,* J. MILLER,* and A. J. PARKER*

[Manuscript received February 28, 1956]

Summary

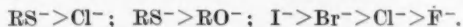
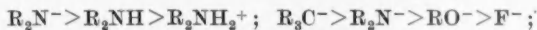
The reactions of a series of phenoxides in MeOH with 1-chloro-2,4-dinitrobenzene (and in one case with picryl chloride also) have been measured. They are compared with each other and with the OMe^- reaction.

The reactions of the several phenoxides show a relationship between basicity and nucleophilicity analogous to the Brønsted relationship between acid-base strength and catalytic activity, but the relationship does not include OMe^- . The phenoxide reactions also obey the Hammett equation with a ρ value similar to those for ionization of phenols in water and alcohols.

General features of nucleophilicity and basicity are discussed in outline.

I. INTRODUCTION

It is a well-known feature of nucleophilic substitutions that over the whole range of substituents the nucleophilicity towards hydrogen ion (i.e. basicity) does not parallel that towards electron deficient centres on carbon and other atoms (Bartlett and Small 1950; Bunnett and Zahler 1951; Hughes 1951; Miller 1951; de la Mare and Vernon 1952; Ingold 1953*a*, pp. 306-408; Leahy and Miller 1953; Swain and Scott 1953; Bunnett and Davis 1954; Edwards 1954). The facility of nucleophilic attack appears to be concerned almost entirely with the simple consideration of the constraint on the electrons which become shared when reaction occurs. In large atoms, as indicated also by polarizability measurements, the increase of constraint due to the increased nuclear charge is more than counteracted by increased distance of valency electrons from the nucleus and inner shell screening. Also to be considered is the increasing effective nuclear charge on moving to the right along a horizontal period of the Periodic Table (Ingold 1953*b*, p. 9). With these considerations in mind orders of nucleophilicity may be predicted, for example,



Basicity, however, appears to involve in addition (or at least to a greater extent) a stereochemical factor favouring small atoms, analogous to that discussed by Ingold (1953*c*, pp. 74-7) (cf. Pitzer 1948) in considering $+M$ effects, and which leads to an inverted order of atoms in vertical groups of the Periodic Table (Dippy and Lewis 1936; Baker and Hopkins 1949; Baker, Barrett, and

* Department of Chemistry, University of Western Australia, Nedlands, W.A.

Tweed 1952; Ingold 1953*b*, p. 9; Heppollette and Miller 1953). Ingold's discussion refers to the ease of (partial) double bond formation, and it is not obvious that the same considerations should apply to the formation of new (single) bonds to electron deficient hydrogen but not other electron deficient centres. A likely explanation is that the overlap of bonding orbitals, possible between the valency electrons of high principal quantum number in large atoms and the uniquely small 1*s* bonding orbital of hydrogen, is considerably less than for other atoms where the constraint on valency electrons then becomes the deciding factor.

Whatever the theoretical explanation it seems that the nucleophilicities of reagents such as I⁻ and RS⁻ towards electron deficient carbon, for example, should not be regarded as abnormally high, but their basicities as abnormally low.

For atoms in the first horizontal period of the Periodic Table, where stereochemical factors related to the size of the nucleophilic atom itself are at a minimum, another steric effect comes into prominence when bulky groups are attached to the nucleophilic atom. There will then be a considerable increase in steric strain consequent on the formation of the bond between nucleophilic and electrophilic centres. This will be at a minimum when the electrophilic centre is hydrogen ion so that basicity is favoured relatively to nucleophilicity by this effect, which is discussed by Brown (1953) as F-strain.

Basicity and nucleophilicity should however run parallel within series of nucleophiles whose members are similar in structure and steric requirements, and this is confirmed by the present work. It is intended to consider the general problem of nucleophilicity quantitatively (cf. Swain and Scott 1953; Edwards 1954) in subsequent papers.

II. RESULTS AND DISCUSSION

Rates of reaction of OMe⁻ and a series of phenoxides in MeOH with 1-chloro-2,4-dinitrobenzene (and/or with picryl chloride), together with various derived quantities are presented in Table 1. The (linear) plots of both activation energy *E* and rate constant log₁₀*k*₂ against the p*K*_{acid} of the several phenols, whose conjugate bases are the nucleophilic reagents, are shown as Figure 1. The Hammett plot, showing a typical linear relationship, of log₁₀*k*₂ against the σ or σ* values (as appropriate) of the phenol substituents is shown as Figure 2 (Hammett 1937, 1938, 1940).

The data of Table 1, where p*K*_{acid} values for phenols are known, may be used to estimate rates and activation energies (frequency factors vary only slightly though consistently) for reactions of phenoxides with 1-chloro-2,4-dinitrobenzene and picryl chloride. If the reasonable assumption is made that substituent effects in the aromatic halogen compound are closely similar for OMe⁻ and phenoxide attack then values of *E* and *k*₂ may also be estimated for the considerable number of compounds whose rates of reaction with OMe⁻ in MeOH have been measured by Miller and co-workers (e.g. Miller and Williams 1953; Heppollette and Miller 1953; Miller 1954; Heppollette, Miller, and Williams 1955; Bolto, Liveris, and Miller 1956*a*; Miller 1956).

TABLE I
REACTION OF OR⁻ IN MEOH WITH (i) 1-CHLORO-2,4-DINITROBENZENE AND (ii) PICRYL CHLORIDE

Reagents	Rate Constants ($10^3 k_2$) (l. mole ⁻¹ sec ⁻¹)		Rate Ratio at 50 °C		<i>E</i> (kcal)	Log ₁₀ <i>B</i>	σ or σ^*	p <i>K</i> _{acid} in MeOH
	At Temperatures shown in Parenthesis	Calculated at 50 °C (log ₁₀ <i>k</i> ₂ shown in brackets)	OMe ⁻ = 1	OPh ⁻ = 1				
OMe ⁻ (i)	See Beckwith, Miller, and Leahy (1952)	28800 [—0.541]	1.00	2.74×10^4	17.4 ₅	11.2 ₅	—	18.07
OPh ⁻ (i)	31.0 92.7 151 265 (15.2) (25.2) (29.9) (35.4)	1050 [—1.978]	3.65×10^{-2}	1.00	18.7 ₅	10.7	0.000	12.82†‡
<i>m</i> -NO ₂ C ₆ H ₄ O ⁻ (i)	86.2 258 1270 (52.2) (64.0) (82.4)	69.3 [—3.159]	2.41×10^{-3}	6.60×10^{-2}	20.4 ₅	10.7	0.710	11.224‡
<i>p</i> -NO ₂ C ₆ H ₄ O ⁻ (i)	60.7 268 605 (82.4) (100.4) (110.7)	2.61 [—4.583]	9.06×10^{-5}	2.49×10^{-3}	22.0 ₅	10.3 ₅	1.270	10.004‡§
(ii)	276 1150 2960 (0.0) (14.5) (25.0)	22000	—	—	15.3 ₅	9.7	—	—
2,4-(NO ₂) ₂ C ₆ H ₃ O ⁻ (ii) (i)*	30.8 111 603 (45.4) (60.2) (81.9)	46.8 0.00555* [—7.256*]	1.93×10^{-78}	5.29×10^{-68}	18.2 ₅ 24.9 ₅ *	9.0 9.6 ₅ *	— 2.644 (See text)	— 6.95†§

* Estimated for reaction with (i) using the relationship for compounds (i) and (ii) with *p*-NO₂C₆H₄O⁻.

† Estimated by addition of 2.85 (see text) to values of p*K*_{acid} in H₂O.

‡ Bordwell and Cooper (1952).

§ Bates and Schwarzenbach (1954).

Some preliminary results for reaction of phenoxides with 1-chloro-2,4-dinitrobenzene (Leahy and Miller 1953) took no account of any concurrent attack by OMe^- in equilibrium with the phenoxides (cf. Mattaar 1922 ; England

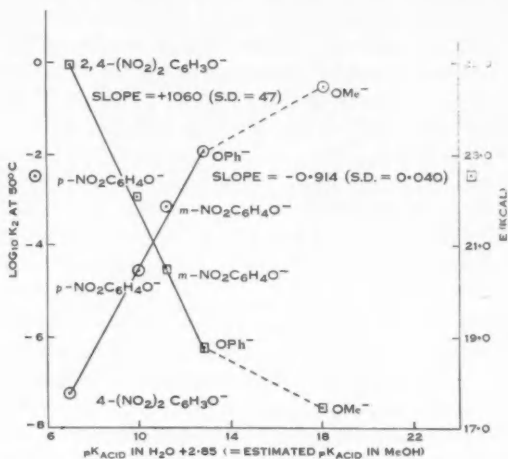


Fig. 1.—Reaction of OR^- in MeOH with 1-chloro-2,4-dinitrobenzene at 50 °C.

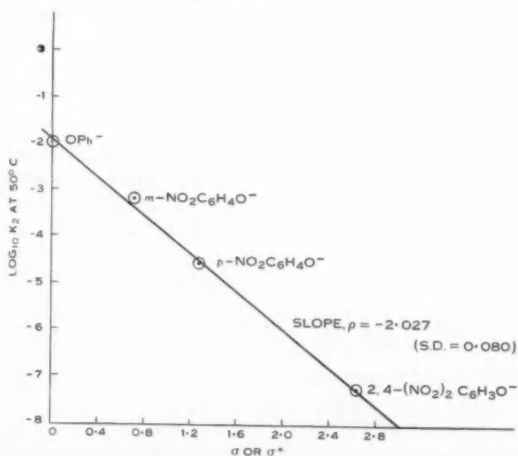


Fig. 2.—Hammett plot for reaction of OAr^- in MeOH with 1-chloro-2,4-dinitrobenzene at 50 °C.

1954). Such attack was regarded as unimportant in comparing the markedly different rates and activation energies of the several phenoxides. In fact, the absolute rates were all affected by a factor of 2-3 at 50 °C, a larger amount

than had been anticipated. The formation of 2,4-dinitroanisole as product, when excess phenol is not also present and reaction is allowed to go to completion, did not affect this conclusion since it was already known (Miller 1951; Beckwith and Miller 1954*a*, 1954*b*; and unpublished data) that the product diaryl ethers would react with any OMe^- present at rates comparable with those for 1-chloro-2,4-dinitrobenzene. In any case, the activation energies were found to vary in a regular and expected manner from that for OMe^- attack, and the E values found then are very similar to the present values. Some of the differences in E and k_2 are regarded as due to difficulties in the original work in following rates by acid-base titrations.

In the present work, concurrent and consecutive methanolysis was avoided by including with each phenoxide a tenfold excess of the corresponding free phenol, thus displacing to the left and to effective completion the equilibrium



That such reactions were avoided was confirmed by the substantially quantitative isolation of the pure diaryl ethers as the sole products in each reaction.

The solvent is thereby a little changed, but even larger molar proportions of water have been shown to have only a small effect in reactions such as this (Lulofs 1901; Baudet 1924; Bolto and Miller, unpublished results). Since the differences between the rates for the several phenoxides are large, the very minor differences between the several MeOH/ArOH solvents may be neglected. Even the greater difference between absolute MeOH and the several MeOH/ArOH solvents taken as a group may be disregarded since the latter were all about 2 mole per cent. ArOH only, and for comparison, in the reaction of OMe^- in MeOH with 1-chloro-2,4-dinitrobenzene, the addition of 2 mole per cent. water changes the rate by less than 2 per cent. (Lulofs 1901; Baudet 1924; Bolto and Miller, unpublished results).

The present work demonstrates a clear relationship between the basicity and nucleophilicity of the phenoxide reagents analogous to that between acidity and basicity and catalytic power (Taylor 1914; Brønsted and Pedersen 1924). The nucleophilicity is correlated with rates ($\log_{10} k_2$ at 50 °C) and activation energies (E) of reaction of the several phenoxides with 1-chloro-2,4-dinitrobenzene, and the basicity with the pK_{acid} of the phenols. In the logarithmic form the relationships including the standard deviations are expressed by equations (1) (at 50 °C) and (2):

$$\log_{10} k_2 = -1.896 - (0.914 \pm 0.040)(9.97 - \text{pK}_{\text{acid}} \text{ in } \text{H}_2\text{O}), \dots (1)$$

$$E = 18830 + (1060 \pm 47)(9.97 - \text{pK}_{\text{acid}} \text{ in } \text{H}_2\text{O}). \dots (2)$$

To see whether even the comparatively minor change from OAr^- to OMe^- is sufficient to invalidate the relationship, it was necessary to estimate either the pK_{acid} of the phenols in MeOH or the pK_{acid} of MeOH in water, or some other solvent in which the acidities of many phenols have been measured. The former was estimated as follows: from the autoprotolysis constant (Doudon 1951) and density (Clifford and Campbell 1951) of MeOH the pK_{acid} of MeOH

in MeOH is 18.07. Applying the acidity ratio MeOH/H₂O in *iso*-C₃H₇OH (Hine and Hine 1953) to MeOH, the pK_{acid} of H₂O in MeOH is calculated as 18.59 as compared with the value in H₂O of 15.74 derived from the autoprotolysis constant of H₂O=14.00 (Edwards 1954). The difference ($\Delta pK_{acid}=2.85$) is taken as applying also to other compounds of structure ROH such as the phenols, and supported by the known ΔpK_{acid} for phenols in water and 95 per cent. EtOH=2.85 (Jaffé 1953).

With this ΔpK_{acid} it was possible to include OMe⁻ on Figure 1 as well as the failure of the basicity and nucleophilicity relationship shown, though as expected the breakdown is not as serious as for greater changes of structure.

In comparing the nucleophilicity of a simple alkoxide such as OMe⁻ with a series of phenoxides the essential feature to be noted is that the conjugation of the unshared electrons on the oxygen with the ring in the phenoxides reduces their availability for nucleophilic attack, giving the nucleophilicity order



where Ar_{yl₂} is electron attracting compared with Ar_{yl₁}. The same argument is used analogously in discussion of the ionization of alcohols and phenols, and one would expect, therefore, that the reaction series considered in the present paper should obey the Hammett relationship with a ρ value similar to those for ionization of phenols in similar solvents (e.g. Bordwell and Cooper 1952; Schwarzenbach and Egli 1934*a*, 1934*b*) if in the rate-determining transition state of the reaction the combination of the electrostatic and (to some unknown extent) partial covalent bond formation between the oxygen of the OAr⁻ and the carbon of the C—Cl bond in ArCl (cf. Bolto and Miller 1956*b*) reduces the conjugation of the oxygen nucleophilic electron pair with the phenoxide ring to the same order as that in phenols. To make the maximum use of the data available for this purpose it is necessary to determine an equivalent σ^* for the 2,4-dinitro-substituent group. The quoted phenol acidities for phenol and *p*-nitrophenol lead to a $\rho=2.220$ for ionization of phenols in water and thus to an equivalent σ^* for 2,4-dinitro=2.644. The Hammett plot is then shown to be a straight line (Fig. 2) and with the equation (3) including the standard deviation (at 50 °C):

$$\log_{10} k_2 = -1.901 - (2.027 \pm 0.080) \sigma \text{ (or } \sigma^*). \dots\dots (3)$$

The above discussion is thus confirmed and the similarity in the two ρ values is in contrast to the results of Parks, Hammond, and Hawthorne (1955), who compared the ρ values for ionization of carboxylic acids with the reactions of the carboxylates with 1-chloro-2,4-dinitrobenzene.

It is of interest to compare the ρ values for ionization of phenols—the value in 95 per cent. EtOH=2.364 quoted by Jaffé (1953) seems most suitable as an example—and for the phenoxides (nucleophilic species) in the reactions discussed in this paper ($\rho=2.027$ at 50 °C), with the ρ values for the aromatic halogen compound (electrophilic species) in such reactions. For reaction with OMe⁻ the ρ value for monosubstituted fluorobenzenes (Miller 1956) is 7.55 at 50 °C, and for 4-substituted 1-chloro-2-nitrobenzenes (which includes 1-chloro-2,4-

dinitrobenzene; Miller 1956) it is 3.90 at 50 °C. The value for the nucleophilic species is lower and this is to be expected since there the substituent effects are relayed to an atom external though attached directly to the ring, whereas in the electrophilic species they are relayed to one of the ring atoms (cf. Heppollette and Miller 1953).

III. EXPERIMENTAL

Runs were carried out using equimolar quantities (0.05M) of aromatic halogen compound and phenoxide, together with a tenfold excess of the corresponding free phenol (≈ 2 mole %). Rate constants k_2 were obtained by graphical plots after estimating Cl^- potentiometrically in aliquots "quenched" in excess dilute chloride-free HNO_3 . Constants were measured at three or more temperatures T over a range of about 25–35 °C for each compound. The Arrhenius parameters (E and $\log_{10} B$) were determined by a least-squares analysis of six or more separately determined values of $\log_{10} k_2$ and $1/T$. The estimated error in $E = \pm 400$ cal and in $\log_{10} B = \pm 0.3$. The standard deviation determined by least squares was always less than this, for example, for 1-chloro-2,4-dinitrobenzene and *m*-nitrophenoxide, $E = 20470 \pm 150$; $\log_{10} B = 10.69 \pm 0.10$.

TABLE 2
REACTION OF 1-CHLORO-2,4-DINITROBENZENE WITH *p*-NITROPHENOXIDE AT 100.4 °C

Time (min)	0	6	10.5	20	30	45
Titration value (ml)	2.78	3.35	3.85	4.66	5.44	6.45
Reciprocal term ..	0.07003	0.07294	0.07570	0.08065	0.08606	0.09425
Time (min)	50.3	82	100	180	203	
Titration value (ml)	6.80	8.35	9.10	11.14	11.63	
Reciprocal term ..	0.09747	0.1148	0.1256	0.1689	0.1842	

Giving k_2 (least squares) $= 2.693 \pm 0.015 \times 10^{-3}$ (l. mole⁻¹ sec⁻¹)

k_2 (graph) $= 2.70 \times 10^{-3}$

A typical run, for 1-chloro-2,4-dinitrobenzene and *p*-nitrophenoxide, is shown as Table 2.

(a) Preparation of Materials

1-Chloro-2,4-dinitrobenzene: The commercial product was recrystallized from MeOH to constant m.p. 50.5 °C. Bishop, Cavell, and Chapman (1952) give 51 °C; LeFèvre and LeFèvre (1950) give m.p. 50–51 °C.

Picryl Chloride: The commercial product was recrystallized from light petroleum to constant m.p. 83 °C. LeFèvre and LeFèvre (1950) give m.p. 83 °C.

Phenol: A.R. phenol was fractionally distilled at reduced pressure and the fraction of b.p. 90–90.5 °C at 25 mm collected. It was stored over CaCl_2 in a desiccator in the dark. Pardee and Weinrich (1944) give b.p. 85 °C at 20 mm.

m-Nitrophenol: The commercial product was recrystallized to constant m.p. 96.5–97.5 °C from dil. HCl. Davies and Hartshorne (1934) give m.p. 96 °C.

p-Nitrophenol: The commercial product was recrystallized to constant m.p. 114 °C from toluene. Davies and Hartshorne (1934) give m.p. 113.5 °C.

2,4-Dinitrophenol: The commercial product was recrystallized from water to constant m.p. 113 °C. McCrone and Kre (1952) give m.p. 114–115 °C. The sodium salt was also prepared by cooling a concentrated solution of the phenol in water after neutralizing with NaOH aq.

(b) Investigation of Products

After separating the excess phenol the sole products obtained from reaction mixtures were the expected (known) diaryl ethers, and these were pure as indicated by melting points of the reaction products before and after recrystallization. The yields in product analysis experiments were 90–95 per cent., and in view of the dilute solutions used, and the necessity to remove tenfold excess of corresponding phenols, this is regarded as a quantitative isolation.

Since 2,4-dinitroanisole has been isolated in quantitative yields by reaction of OMe⁻ in MeOH with 1-chloro-2,4-dinitrobenzene (Beckwith, Miller, and Leahy 1952), it is felt in any case, that if any dinitro- or trinitroanisole had been formed concurrently they would have shown up as impurities in the precipitated ethers.

It is already known that the dinitrophenoxy group in polynitrodiaryl ethers is replaced considerably more readily than is similarly situated chlorine (Beckwith and Miller, unpublished data), and therefore, that 2,2',4,4',6-penta-nitrodiphenyl ether (formed from sodium dinitrophenoxide and picryl chloride) would probably react with the solvent. Investigation of the literature shows that this has been recorded (Desvergues 1926).

IV. ACKNOWLEDGMENT

One of us (A.J.P.) wishes to express his gratitude to C.S.I.R.O. for a studentship.

V. REFERENCES

- BAKER, J. W., BARRETT, G. F. C., and TWEED, W. T. (1952).—*J. Chem. Soc.* **1952**: 2831.
BAKER, J. W., and HOPKINS, H. B. (1949).—*J. Chem. Soc.* **1949**: 1089.
BARTLETT, P. D., and SMALL, G. (1950).—*J. Amer. Chem. Soc.* **72**: 4867.
BATES, R. G., and SCHWARZENBACH, G. (1954).—*Helv. Chim. Acta* **37**: 1069.
BAUDET, H. P. (1924).—*Rec. trav. Chim.* **43**: 707.
BECKWITH, A. L., and MILLER, J. (1954a).—*J. Org. Chem.* **19**: 1416.
BECKWITH, A. L., and MILLER, J. (1954b).—*J. Org. Chem.* **19**: 1708.
BECKWITH, A. L., MILLER, J., and (in part) LEAHY, G. D. (1952).—*J. Chem. Soc.* **1952**: 3552.
BISHOP, R. R., CAVELL, E. A. S., and CHAPMAN, N. B. (1952).—*J. Chem. Soc.* **1952**: 437.
BOLTO, B. A., LIVERIS, M., and MILLER, J. (1956a).—*J. Chem. Soc.* **1956**: 750.
BOLTO, B. A., and MILLER, J. (1956b).—*Aust. J. Chem.* **9**: 74.
BORDWELL, F. G., and COOPER, G. D. (1952).—*J. Amer. Chem. Soc.* **74**: 1058.
BRONSTED, J. N., and PEDERSEN, K. (1924).—*Z. physik. Chem.* **108**: 185.
BROWN, H. C. (1953).—*Rec. Chem. Progr.* **14**: 83.
BUNNETT, J. F., and DAVIS, G. T. (1954).—*J. Amer. Chem. Soc.* **76**: 3011.
BUNNETT, J. F., and ZAHLER, R. E. (1951).—*Chem. Rev.* **49**: 271.
CLIFFORD, G., and CAMPBELL, J. A. (1951).—*J. Amer. Chem. Soc.* **73**: 5449.
DAVIES, E. S., and HARTSHORNE, N. H. (1934).—*J. Chem. Soc.* **1934**: 1830.
DESVERGNES, L. (1926).—*Monit. Sci.* (5) **16**: 204.
DIPPY, J. F. J., and LEWIS, R. H. (1936).—*J. Chem. Soc.* **1936**: 644.

- DOUDON, M. L. (1951).—*J. Chim. Phys.* **48**: C27.
- EDWARDS, J. O. (1954).—*J. Amer. Chem. Soc.* **76**: 1540.
- ENGLAND, B. D. (1954).—*Chem. & Ind.* **1954**: 1145.
- HAMMETT, L. P. (1937).—*J. Amer. Chem. Soc.* **59**: 96.
- HAMMETT, L. P. (1938).—*Trans. Faraday Soc.* **34**: 156.
- HAMMETT, L. P. (1940).—“Physical Organic Chemistry.” pp. 186–8. (McGraw-Hill Book Co. Inc.: New York.)
- HEPPOLETTE, R. L., and MILLER, J. (1953).—*J. Amer. Chem. Soc.* **75**: 4265.
- HEPPOLETTE, R. L., MILLER, J., and WILLIAMS, V. A. (1955).—*J. Chem. Soc.* **1955**: 2929.
- HINE, J., and HINE, M. (1952).—*J. Amer. Chem. Soc.* **74**: 5266.
- HUGHES, E. D. (1951).—*Quart. Rev.* **5**: 245.
- INGOLD, C. K. (1953).—“Structure and Mechanism in Organic Chemistry.” (G. Bell & Sons Ltd.: London.)
- JAFFÉ, H. H. (1953).—*Chem. Rev.* **53**: 191.
- LEAHY, G. D., and MILLER, J. (1953).—*Chem. & Ind.* **1953**: 40.
- LEFÈVRE, C. G., and LEFÈVRE, R. J. W. (1950).—*J. Chem. Soc.* **1950**: 1829.
- LULOFS, P. K. (1901).—*Rec. trav. Chim.* **20**: 292.
- DE LA MARE, P. B., and VERNON, C. A. (1952).—*J. Chem. Soc.* **1952**: 3331.
- MCCRONE, W., and KRC, J., JR. (1952).—*Anal. Chem.* **24**: 1863.
- MATTAAR, T. J. F. (1922).—*Rec. trav. Chim.* **41**: 101.
- MILLER, J. (1951).—*Rev. Pure Appl. Chem.* **1**: 171.
- MILLER, J. (1954).—*J. Amer. Chem. Soc.* **76**: 448.
- MILLER, J. (1956).—*Aust. J. Chem.* **9**: 61.
- MILLER, J., and WILLIAMS, V. A. (1953).—*J. Chem. Soc.* **1953**: 1475.
- PARDEE, W. A., and WEINRICH, W. (1944).—*Industr. Engng. Chem.* **36**: 595.
- PARKS, L. R., HAMMOND, G. S., and HAWTHORNE, M. F. (1955).—*J. Amer. Chem. Soc.* **77**: 2903.
- PITZER, K. S. (1948).—*J. Amer. Chem. Soc.* **70**: 2140.
- SCHWARZENBACH, G., and EGLI, H. (1934a).—*Helv. Chim. Acta* **17**: 1176.
- SCHWARZENBACH, G., and EGLI, H. (1934b).—*Helv. Chim. Acta* **17**: 1183.
- SWAIN, C. G., and SCOTT, C. B. (1953).—*J. Amer. Chem. Soc.* **75**: 141.
- TAYLOR, H. S. (1914).—*Z. Elektrochem.* **20**: 201.

THE REACTION OF SODIUM ACETYLIDE WITH BENZIL AND RELATED COMPOUNDS

By J. CYMERMAN-CRAIG,* M. MOYLE,* PAMELA ROWE-SMITH,*
and P. C. WAILES*

[Manuscript received October 27, 1955]

Summary

Attempted condensation of benzil and benzoin with sodium acetylide in liquid ammonia caused fission of the central carbon-carbon bond of these substances, giving 3-phenylprop-1-yn-3-ol.

Condensation of α -bromodeoxyanisoin with the same reagent gave several non-acetylenic products which have been identified.

I. INTRODUCTION

An extensive literature (cf. Johnson 1946) considered the condensation of acetylene with carbonyl compounds, but few such condensations with dicarbonyl compounds have been reported. Aliphatic diketones have been shown to condense normally with acetylene (Milas, Brown, and Phillips 1948), 1-hexyne (Cymerman and Rowe-Smith 1949), and phenylacetylene (Wilson and Hyslop 1923, 1924); and Kleinfeller and Eckert (1929) prepared the acetylenic glycol from benzil and acetylenedimagnesium bromide. The condensation of aromatic diketones with acetylene itself, not previously investigated, was of interest because of the relationship of the expected products to the synthetic oestrogens of Dodds *et al.* (1939).

Attempted condensation of benzil and sodium acetylide in liquid ammonia resulted in fission of the benzil molecule giving benzoic acid, benzamide, and an acetylenic product identified as 3-phenylprop-1-yn-3-ol. A similar attempted condensation using ether as solvent gave only benzilic acid, also obtained from benzil and acetylene in the presence of potassium *tert.*-amyloxide. Kasiwagi (1926) obtained benzilic acid by reaction of sodamide and benzil in toluene.

Treatment of benzil with liquid ammonia alone gave only a trace of benzamide, but treatment with sodamide in liquid ammonia gave both benzamide and benzoic acid, as well as *N*- α -dibenzoylbenzylamine (I), previously reported by Henius (1885) from the action of ammonia on benzil, and synthesized by Davidson, Weiss, and Jelling (1937).

Benzoin condenses normally with both acetylenedimagnesium bromide (Zalkind and Komarovskaia 1927) and phenylacetylenylmagnesium bromide (Zalkind and Martinson 1936). Reaction of benzoin with sodium acetylide in liquid ammonia gave benzoic acid and 3-phenylprop-1-yn-3-ol. A non-

* Department of Organic Chemistry, University of Sydney.

volatile neutral product ($C_{10}H_8O$)_n is probably a di- α -hydroxybenzylidiphenylfuran such as II, formed by dehydration and rearrangement (cf. Kleinfeller 1939) of the acetylenic tetrol previously obtained by Zalkind and Komarovskaia (1927). Liquid ammonia alone had no action on benzoin. Fission of the carbon chain in benzil and benzoin by ammonia under more vigorous conditions has been reported previously to give benzaldehyde, benzoic acid, and benzamide (Japp and Wynne 1886; Kharasch, Sternfeld, and Mayo 1940; Leslie and Watt 1942).

Condensation of α -bromodeoxyanisoin (Cymerman-Craig, Martin, and Wailes 1955) with sodium acetylide in liquid ammonia gave anisic acid, showing that molecular fission had again occurred. Anisoin was isolated from the ketonic portion of the neutral fraction after treatment with Girard P reagent (Girard and Sandulesco 1936) while the non-ketonic fraction yielded a substance $C_{18}H_{18}O_4$, showing an absorption maximum at 2840 Å in the ultraviolet region. A positive iodoform reaction and the presence of 0.4 active hydrogen atom (Zerewitinoff) were in agreement with the structure 1,2-di-(*p*-methoxyphenyl)-butan-1,3-dione (III), and reaction with hydroxylamine afforded deoxyanisoin oxime. Wittig, Bangert, and Kleiner (1928) report similar detachment of an acetyl group from 1,2-diphenylbutan-1,3-dione, and Russell and Csendes (1954) report the spectrum of the similarly-constituted α -formyldeoxybenzoin to resemble that of deoxybenzoin. The product III was not identical with the isomeric deoxyanisoin enol acetate (Barnes *et al.* 1943), which had m.p. 90 °C and gave a negative iodoform test. It is difficult to envisage the formation of III other than by hydration of an ethynyl group. Reaction of deoxyanisoin with acetyl chloride or bromide in the presence of sodamide or magnesium was unsuccessful. Condensation of anisoyl chloride with sodio ethyl acetoacetate gave ethyl 1-anisoyl-2-keto-butyrate which could however not be induced to condense with *p*-iodoanisole.

Attempted condensation of *p*-methoxyphenyl acetone with anisoyl chloride, or with ethyl anisoate, using sodium ethoxide, ethylmagnesium bromide, or sodamide as catalysts, did not give the 1,3-diketone.

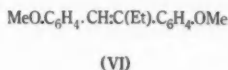
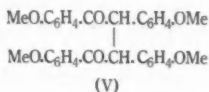
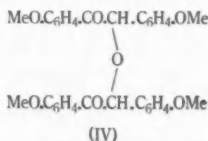
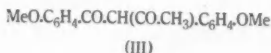
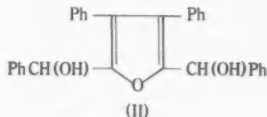
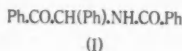
Chromatography of the non-volatile residue of the non-ketonic fraction gave two crystalline products: bis-(α -anisoyl-4-methoxybenzyl) ether (IV), and 1,2,3,4-tetra-(*p*-methoxyphenyl)butan-1,4-dione (V), also formed in a Wurtz side reaction occurring on attempted interaction of α -bromodeoxyanisoin with the sodium salt of anisoin.

Although excess of Girard P reagent was used in the separation, the 1,3-diketone (III), the diketether (IV) and the 1,4-diketone (V) were all isolated from the "non-ketonic" fraction. No previous case of the failure of diketones to react with Girard P reagent has come to our notice.

Reaction of excess of ethylmagnesium bromide with α -bromodeoxyanisoin did not give the desired diethyl stilboestrol dimethyl ether. The main product was deoxyanisoin, together with 1,2,3,4-tetra-(*p*-methoxyphenyl)butan-1,4-dione (V) and 1,2-di-(*p*-methoxyphenyl)-1-butene (VI). Reductive dehalogenation of α -bromoketones by Grignard reagents has been observed by Fisher,

Oakwood, and Fuson (1930), Kohler and Tishler (1932), and Lutz and Reveley (1941), and VI is clearly produced by reaction of excess Grignard reagent with the deoxyanisoin so formed, followed by dehydration. VI has been previously reported by Dodds *et al.* (1939) using the latter method.

Attempted condensation of anisil with 1 or 4 mol of propargyl alcohol, as its dimagnesium bromide complex (Zeile and Meyer 1942), gave only anisoin (15 per cent.). The facile reduction of anisil by Grignard reagents has been previously noted (Dodds *et al.* 1939).



II. EXPERIMENTAL

All known products were identified by m.p. and mixed m.p.

(a) *Attempted Condensation of Benzil and Sodium Acetylide.*—(i) A solution of benzil (21 g; 0.1 mol) in benzene (150 ml) was added during 1 hr to a vigorously stirred and cooled solution of sodium acetylide (from 11.5 g of Na) in liquid ammonia (1 l.). Stirring was continued for 6.5 hr with continued slow passage of acetylene. After addition of ammonium chloride (30 g), the ammonia was allowed to evaporate and the residue treated with ice-water, acidified with sulphuric acid (2N), and extracted with benzene. The aqueous layer was basified (sodium hydroxide solution) and extracted with chloroform. The extracts afforded benzamide (3.85 g, 16% yield). The benzene extracts were washed (sodium bicarbonate solution) and the bicarbonate washings acidified and extracted with benzene, giving benzoic acid (6 g, 25% yield). No benzilic acid was detected.

The original benzene extract on distillation gave 3-phenylprop-1-yn-3-ol (1 g, 4% yield) as a pale yellowish mobile liquid, n_D^{19} 1.5514 (Found: C, 82.3; H, 6.3%; active H (Zerewitinoff): 1.9 active H atoms per mol. Calc. for $\text{C}_9\text{H}_8\text{O}$: C, 81.8; H, 6.1%; 2 active H atoms per mol). It was identified in the manner described in Section II (d).

The solid residue (5.25 g) from the original distillation of the neutral fraction gave no precipitate with Tollens's reagent, and attempted purification gave only material of wide m.p. range (100–235 °C).

(ii) A solution of sodium acetylide (from 11.5 g of Na) in liquid ammonia (300 ml) was prepared and the ammonia allowed to evaporate and be replaced by ether (300 ml). Passage of acetylene was continued, and benzil (10.5 g; 0.05 mol) in ether (120 ml) added during 0.5 hr followed by stirring for a further 3 hr. Working up gave an acidic fraction containing only benzilic acid (4.4 g, 38.5% yield), and a neutral fraction consisting of unchanged benzil (4.7 g, 45% recovery). No alkaline fraction was obtained.

(iii) Ether (150 ml) saturated with acetylene at -15°C was treated simultaneously with a solution of benzil (10.5 g; 0.05 mol) in benzene (50 ml) and a solution of potassium (4 g; 0.1 mol) in *tert.*-amyl alcohol (50 ml) added over 0.75 hr with vigorous stirring. After a further 4 hr stirring at -15°C , working up gave benzoic acid (8.1 g, 71% yield) as sole product.

(b) *Reaction of Benzil with Liquid Ammonia*.—A solution of benzil (11.3 g) in benzene (100 ml) was added to liquid ammonia (500 ml) and the mixture stirred for 3.5 hr. Working up gave a basic fraction of benzamide (0.15 g, 1.5% yield), and a neutral fraction of benzil (9.1 g, 81% recovery). No acidic fraction was obtained.

(c) *Reaction of Benzil with Sodamide in Liquid Ammonia*.—A solution of benzil (14 g; 0.07 mol) in benzene (250 ml) was added to sodamide (2.7 g; 0.07 mol) in liquid ammonia (500 ml). A pink colour developed; stirring was continued for 3 hr and the mixture worked up as described above.

The alkaline portion gave benzamide (0.95 g, 6% yield), and the acidic fraction yielded benzoic acid (1.5 g, 9.5%). The neutral fraction gave benzil (8.6 g, 61.5% recovery), and a neutral solid, which recrystallized from a large volume of ethanol as white crystals, m.p. 135°C (2.2 g, 21% yield), of *N*- α -dibenzoylbenzylamine (Found: N, 4.5%. Calc. for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$: N, 4.4%). Henius (1885) gives m.p. 137 – 139°C .

(d) *Condensation of Benzoin with Sodium Acetylide*.—Benzoin (53 g; 0.25 mol) was added during 1 hr to a solution of sodium acetylide (from 18 g of Na) in liquid ammonia (1 l.) and the mixture stirred for a further 2.5 hr. Benzene (100 ml) and ammonium chloride (50 g) were added and the mixture worked up as described above.

The acidic portion afforded benzoic acid (5 g, 8% yield). No basic fraction was obtained. The neutral extracts on distillation gave 3-phenylprop-1-yn-3-ol (10 g, 16% yield) as a pale yellowish oil, n_{D}^{24} 1.5494 (Found: C, 81.7; H, 6.4%; active H (Zerewitinoff): 1.8 active H atoms per mol). It showed only end-absorption in the ultraviolet region. On standing, the substance solidified to prisms, m.p. 32.5 – 33.5°C . Clapperton and MacGregor (1949) give for 3-phenylprop-1-yn-3-ol, m.p. 29 – 30°C , n_{D}^{20} 1.5511.

The product (5 g) was hydrogenated in ethyl acetate solution in the presence of platinum oxide, absorbing 3.8 hydrogen atoms per mol. Working up gave 1-phenylpropanol (4.5 g, 90% yield), b.p. $82^{\circ}\text{C}/2$ mm, n_{D}^{25} 1.5182 (Found: C, 79.2; H, 9.1%; active H (Zerewitinoff): 1.05 active H atoms per mol. Calc. for $\text{C}_9\text{H}_{12}\text{O}$: C, 79.4; H, 8.9%; 1 active H atom per mol). Klages (1903) gives b.p. 108 – $110^{\circ}\text{C}/15$ mm. Oxidation of 1-phenylpropanol with chromic acid gave propiophenone, characterized as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 189 – 190°C (Found: N, 17.4%. Calc. for $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_4$: N, 17.7%). The semicarbazone had m.p. 174 – 175°C . Stobbe and Niedenzu (1902) report m.p. 173 – 175°C .

The residue remaining after distillation of the neutral fraction solidified on trituration with cold ethanol, affording a solid (15 g, 28% yield). Crystallization from chloroform-light petroleum (b.p. 60 – 90°C) gave yellow microcrystals, probably 2,5-di-(α -hydroxybenzyl)-3,4-diphenylfuran, m.p. 195 – 196°C (decomp.) after shrinking at 185°C (Found: C, 83.3; H, 5.5%; active H (Zerewitinoff): 1.8 active H atoms per mol. Calc. for $\text{C}_{30}\text{H}_{24}\text{O}_3$: C, 83.3; H, 5.5%; 2 active H atoms per mol). The substance gave no reaction with Tollens's reagent and was recovered unchanged from attempted glycol fission in acetic acid solution using either sodium bismuthate or lead tetra-acetate.

(e) *Reaction of α -Bromodeoxyanisoin with Sodium Acetylide*.—A solution of α -bromodeoxyanisoin (22.5 g; 0.067 mol) in benzene (200 ml) was added during 0.5 hr to a solution of sodium acetylide (from 9 g of Na; 0.39 mol) in liquid ammonia (1 l.) and the orange mixture stirred for 5 hr. On working up in the usual manner, no basic fraction was obtained; the acidic portion was anisic acid (2.2 g, 21.5% yield).

The neutral fraction (15.3 g) was treated with Girard P reagent. The ketonic portion (1 g, 5.5% yield) was anisoin, and the non-ketonic fraction (11 g) on distillation gave an oil, b.p. c. 185 – $190^{\circ}\text{C}/0.07$ mm, solidifying and crystallizing from methanol as pale yellow needles (1.5 g, 7.5% yield) of 1,2-di-(*p*-methoxyphenyl)butan-1,3-dione, m.p. 96 – 97°C (Found: C, 72.8;

H, 6.0; CH_2O , 21.6%. Calc. for $\text{C}_{15}\text{H}_{18}\text{O}_4$: C, 72.5; H, 6.1; $2\text{CH}_2\text{O}$, 20.9%). The substance gave a strong iodoform reaction, and with 2,4-dinitrophenylhydrazine gave an orange solid, m.p. 152–153 °C. Active H (Zerewitinoff): the compound (0.043 g) evolved 1.5 ml of methane at 25 °C/763 mm, corresponding to 0.4 active H atom per mol. Treatment of the compound with hydroxylamine hydrochloride and sodium hydroxide for 1 hr gave deoxyanisoin oxime, m.p. 120.5–121 °C (Found: C, 70.9; H, 6.3; N, 5.4%. Calc. for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}$: C, 70.8; H, 6.3; N, 5.2%). A mixed m.p. with an authentic specimen was undepressed. Dankova *et al.* (1951) give m.p. 118–120 °C.

The non-distillable residue was dissolved in benzene-light petroleum and passed through a column of alumina, giving a solid (0.5 g, 3% yield) crystallizing from methanol as white needles, m.p. 156 °C, of *bis*-(α -anisoyl-4-methoxybenzyl) ether (Found: C, 73.1; H, 6.0%; mol. wt. (Rast), 510. Calc. for $\text{C}_{32}\text{H}_{36}\text{O}_7$: C, 73.0; H, 5.8%; mol. wt., 526).

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA IN 95 PER CENT. ETHANOL

Compound	λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}
Anisoin	2200 2770	24,000 21,500	2420	3900
Deoxyanisoin	2200 2770	24,000 22,000	2390	3000
Bis-(α -anisoyl-4-methoxybenzyl) ether (IV)	2200 2810	44,500 39,000	2420	9000
1,2,3,4 - Tetra - (<i>p</i> - methoxyphenyl)- butan-1,4-dione (V)	2200 2820	45,500 42,500	2420	9200
1,2 - Di - (<i>p</i> - methoxyphenyl)butan - 1,3-dione (III)	c. 2200 2820	c. 18,500 21,000	2400	4700
1,2-Di-(<i>p</i> -methoxyphenyl)ethanol ..	2270 2740	24,000 6,500	2440	1850
<i>p</i> -Methoxyacetophenone (Morton and Stubbs 1940)	2190 2770	11,700 14,800	2400	900

The mother liquors from which the preceding compound had separated yielded another substance (0.02 g) crystallizing from benzene-light petroleum as colourless plates, m.p. 208 °C, of 1,2,3,4-tetra-(*p*-methoxyphenyl)butan-1,4-dione (Found: C, 75.0; H, 6.1%. Calc. for $\text{C}_{22}\text{H}_{26}\text{O}_6$: C, 75.2; H, 5.9%).

(f) *Attempted Synthesis of Bis-(α -anisoyl-4-methoxybenzyl) Ether.*—After addition of anisoin (2 g) in toluene (30 ml) to molten sodium (0.17 g; 1 mol) under toluene (20 ml), α -bromo-deoxyanisoin (2.4 g) in toluene (40 ml) was added, and heating continued for 0.5 hr. The mixture was filtered, the filtrate evaporated, and the residue crystallized from methanol, affording only anisil and deoxyanisoin. The methanol-insoluble portion (0.05 g) crystallized from benzene-light petroleum as white needles, m.p. 206–207 °C, of 1,2,3,4-tetra-(*p*-methoxyphenyl)butan-1,4-dione, undepressed on admixture with the product obtained in Section II (e).

(g) *Attempted Synthesis of 1,2-Di-(p-methoxyphenyl)butan-1,3-dione.*—Sodium ethyl acetoacetate (from 10 g of ethyl acetoacetate) in benzene was treated with anisoyl chloride (13.1 g; 1 mol), and the mixture refluxed for 3 hr. Working up gave the alkali-soluble ethyl 1-anisoyl-



2-ketobutyrate as an oil, b.p. 132 °C/0.05 mm (Found : C, 63.6; H, 6.3%. Calc. for $C_{14}H_{16}O_5$: C, 63.6; H, 6.1%).

(h) Reaction of α -Bromodeoxyanisoin with Ethylmagnesium Bromide.— α -Bromodeoxyanisoin (8 g; 0.024 mol) in toluene (50 ml) was added to ethylmagnesium bromide (from 2.32 g of Mg; 0.096 mol) in ether (50 ml), and the solution refluxed for 7 hr. Working up gave deoxyanisoin (3.7 g, 60.5% yield) as the least soluble fraction. Treatment of the remainder with Girard P reagent gave a ketonic fraction containing more deoxyanisoin (0.8 g). The non-ketonic portion was a yellow oil (0.8 g) which dissolved in light petroleum (b.p. 40–70 °C) leaving an insoluble solid (0.1 g), m.p. 204–206 °C, undepressed on admixture with 1,2,3,4-tetra-(*p*-methoxyphenyl)butan-1,4-dione prepared in Section II (e).

The yellow oil (0.7 g, 11% yield) obtained on evaporation of the light petroleum filtrate, immediately decolorized bromine water and was identified as 1,2-di-(*p*-methoxyphenyl)-1-butene by ozonolysis.

The oil was dissolved in ethyl acetate (25 ml) and treated with ozonized oxygen for 20 min. Decomposition of the ozonide with zinc dust and boiling water, followed by ether extraction, gave a viscous product (0.64 g). Treatment with 2,4-dinitrophenylhydrazine and purification of the product on a column of alumina gave 2 fractions: (i) blood-red prisms, m.p. 187 °C, undepressed on admixture with the derivative of *p*-methoxypropiphenone; (ii) orange needles, m.p. 248 °C, not depressed with the derivative of anisaldehyde.

Light Absorption.—Ultraviolet spectra were determined in 95% ethanol solution using a Unicam S.P. 500 spectrophotometer and are recorded in Table I.

III. REFERENCES

- BARNES, R. P., COOPER, S. R., TULANE, V. J., and DELANEY, H. (1943).—*J. Org. Chem.* **8** : 153.
CLAFFERTON, E. T. and MACGREGOR, W. S. (1949).—*J. Amer. Chem. Soc.* **71** : 3234.
CYMERMAN, J., and ROWE-SMITH, P. (1949).—*J. Chem. Soc.* **1949** : 3368.
CYMERMAN-CRAIG, J., MARTIN, K. V., and WAILES, P. C. (1955).—*Aust. J. Chem.* **8** : 385.
DANKOVA, T. F., BOKOVA, T. N., PREOBRAZHENSKI, N. A., PETRUSHCHENKO, A. E., ILSTEIN, I. A., and SHVETSOV, N. I. (1951).—*J. Gen. Chem. U.S.S.R.* **21** : 787.
DAVIDSON, D., WEISS, M., and JELLING, M. (1937).—*J. Org. Chem.* **2** : 319.
DODDS, E. C., GOLBERG, L., LAWSON, W., and ROBINSON, R. (1939).—*Proc. Roy. Soc. B* **127** : 140.
FISHER, C. H., OAKWOOD, T. S., and FUSON, R. C. (1930).—*J. Amer. Chem. Soc.* **52** : 5036.
GIRARD, A., and SANDULESCO, G. (1936).—*Helv. Chim. Acta* **19** : 1095.
HENIUS, M. (1885).—*Liebigs Ann.* **228** : 339.
JAPP, F. R., and WYNNE, W. P. (1886).—*J. Chem. Soc.* **49** : 473.
JOHNSON, A. W. (1946).—"The Chemistry of the Acetylenic Compounds." (E. Arnold : London.)
KASIWAGI, I. (1926).—*Bull. Chem. Soc. Japan* **1** : 66.
KHARASCH, M. S., STERNFELD, E., and MAYO, F. R. (1940).—*J. Org. Chem.* **5** : 362.
KLAGES, A. (1903).—*Ber. dtsh. chem. Ges.* **36** : 621.
KLEINFELLER, H. (1939).—*Ber. dtsh. chem. Ges.* **72** : 249.
KLEINFELLER, H., and ECKERT, F. (1929).—*Ber. dtsh. chem. Ges.* **62** : 1598.
KOHLE, E. P., and TISHLER, M. (1932).—*J. Amer. Chem. Soc.* **54** : 1594.
LESLIE, W. B., and WATT, G. W. (1942).—*J. Org. Chem.* **7** : 73.
LUTZ, R. E., and REVELEY, W. G. (1941).—*J. Amer. Chem. Soc.* **63** : 3180.
MILAS, N. A., BROWN, R. J., and PHILLIPS, O. (1948).—*J. Amer. Chem. Soc.* **70** : 2862.
MORTON, R. A., and STUBBS, A. L. (1940).—*J. Chem. Soc.* **1940** : 1347.
RUSSELL, P. B., and CSENDES, E. (1954).—*J. Amer. Chem. Soc.* **76** : 5714.
STOBBE, H., and NIEDENZU, K. (1902).—*Liebigs Ann.* **321** : 102.
WILSON, F. J., and HYSLOP, W. M. (1923).—*J. Chem. Soc.* **1923** : 2612.
WILSON, F. J., and HYSLOP, W. M. (1924).—*J. Chem. Soc.* **1924** : 1556.
WITTIG, G., BANGERT, F., and KLEINER, H. (1928).—*Ber. dtsh. chem. Ges.* **61** : 1142.
ZALKIND, Y., and KOMAROVSKAIA, E. (1927).—*Ber. dtsh. chem. Ges.* **60** : 182.
ZALKIND, Y. S., and MARTINSON, E. E. (1936).—*J. Gen. Chem. U.S.S.R.* **6** : 1085.
ZEILE, K., and MEYER, H. (1942).—*Ber. dtsh. chem. Ges.* **75** : 356.

CHEMICAL CONSTITUTION AND ANTHELMINTIC ACTIVITY

III. PREPARATION OF SUBSTITUTED PHENOTHIAZINES AND SOME MONO- AND DICYCLIC ANALOGUES

By J. CYMERMAN-CRAIG,* W. P. ROGERS,† and M. E. TATE*

[Manuscript received April 6, 1956]

Summary

A number of alkoxy- and chlorophenothiazines have been prepared. A simple synthesis of 1,4-thiazane is described, and improved methods of preparation of 1-benzyl- and 1-benzoylpiperazine have been developed and used in the preparation of some monosubstituted piperazines.

I. INTRODUCTION

In Part II of this series (Cymerman-Craig, Rogers, and Warwick 1955) the preparation of some derivatives of phenothiazine (I) was described. Several of these, particularly 3-methoxy- and 3-chlorophenothiazine, were found to possess appreciable anthelmintic activity (Cymerman-Craig, Rogers, Tate, and Warwick, unpublished data) and a number of alkoxy- and chlorophenothiazines were therefore prepared to examine the variation of activity with the nature and position of the substituent in this series.

1-Methoxy-, 1-ethoxy-, and 3-ethoxyphenothiazine were prepared from the appropriate diphenylamine and sulphur. This reaction applied to 3-methoxydiphenylamine gave a mixture of 2- and 4-methoxyphenothiazine, the 2-isomer being formed in greater yield. After this work had been substantially completed, the paper of Charpentier *et al.* (1952) came to hand; these authors obtained only the 2-isomer. In the case of 3-chlorodiphenylamine, our results agreed with those of Charpentier *et al.* (1952) in giving both the 2- and 4-isomer, the former preponderating in the ratio of 7:1. Sulphur fusion of 3-chloro-4'-methoxydiphenylamine gave 2-chloro- and 4-chloro-7-methoxyphenothiazine in the ratio of 15:1.

It appears that 2- or 3-monosubstituted phenothiazines have m.p.'s in the range 160–200 °C, while their 1- or 4-substituted isomers melt in the region of 100–120 °C (for m.p.'s see Massie 1954). This order of m.p.'s is retained in disubstituted phenothiazines. In one case (Charpentier *et al.* 1952) this empirical allocation of the orientation has been confirmed by conversion to the corresponding known carbazole.

Smith (1950) showed that sulphur fusion of 3-trifluoromethyldiphenylamine gave a high-melting product which showed infra-red absorption at 826 cm^{-1}

* Department of Organic Chemistry, University of Sydney.

† Department of Zoology, University of Adelaide.

(1,2,4-trisubstituted benzene) and to which he accordingly assigned the structure of a 2-substituted phenothiazine. The infra-red spectra of our compounds in the range $700\text{--}900\text{ cm}^{-1}$ confirm the structures assigned on the basis of the m.p.'s and relative abundance of the isomers (Table 1), 1,2,4-substituted compounds possessing a strong band in the region $808\text{--}832\text{ cm}^{-1}$, while 1,2,3-substituted derivatives showed instead two narrow bands in the range $750\text{--}786\text{ cm}^{-1}$. Both types of band occur in 4-chloro-7-methoxyphenothiazine. The expected shift of the bands to higher frequencies thus takes place when the number of unsubstituted adjacent hydrogen atoms on the benzene rings is reduced.

Fusion with sulphur of 3',5-dichlorodiphenylamine-2-carboxylic acid was accompanied by decarboxylation and gave two isomeric dichlorophenothiazines in the ratio of 4:1, which were allocated the structures 2,8- and 2,6-dichloro-

TABLE 1
INFRA-RED SPECTRA* OF PHENOTHIAZINES IN THE RANGE $700\text{--}900\text{ cm}^{-1}$

Compound	Melting Point (°C)	Maximum (cm^{-1})
2-Chlorophenothiazine	199.5	808
4-Chlorophenothiazine	111	750, 774
2-Chloro-7-methoxyphenothiazine	175.5	823
4-Chloro-7-methoxyphenothiazine	118	774, 786 809
2,8-Dichlorophenothiazine ..	267.5	809
2,6-Dichlorophenothiazine ..	139.5	758, 766 832

* Determined in carbon disulphide solution.

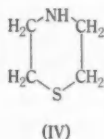
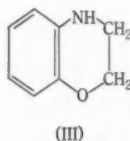
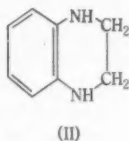
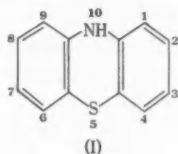
phenothiazine from their m.p.'s and infra-red spectra. No trace of the third possible isomer (4,6-dichlorophenothiazine) was found; no 4,6-disubstituted phenothiazine is known.

Both phenothiazone and 3-hydroxyphenothiazine were advantageously purified by vacuum sublimation, recrystallization having proved unsatisfactory. Reductive acetylation of phenothiazone by a modification of the method of Houston, Kester, and DeEds (1949) gave 3-acetoxyphenothiazine.

Two phenothiazine analogues containing two fused rings were required. Lithium aluminium hydride reduction of 2,3-dihydroxyquinoxaline gave 1,2,3,4-tetrahydroquinoxaline (II) and the same reagent afforded 2,3-dihydro-1,4-benzoxazine (III) from 1,4-benzoxazin-2-one, obtained by a modification of the method of Jacobs and Heidelberger (1917).

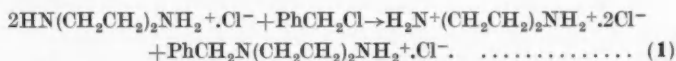
1,4-Thiazane (IV) was of interest because of its relation to the central part of the phenothiazine molecule. Langlet (1896) obtained this compound in unstated yield from 1,2-dibromoethane and 2-aminoethanethiol, and Davies (1920) and recently Cragoe and Hamilton (1945), in 30 per cent. yield from

di-2-chloroethyl sulphide and ammonia. 1,4-Thiazane was however readily obtained in 66 per cent. overall yield from di-2-hydroxyethylamine by reaction of di-2-chloroethylamine hydrochloride with sodium sulphide, and was characterized as the acetate. After this work had been completed, Sommers and Horrom (1954) reported the preparation of IV by lithium aluminium hydride reduction of 3-oxo-1,4-thiazane (obtainable from ethyleneimine and ethyl mercaptoacetate), and Idson and Spoerri (1954) prepared a *C*-methylated 1,4-thiazane by a method similar to that described in the present paper.



In view of the known anthelmintic activity of piperazine, it was of interest to examine a number of monosubstituted derivatives of this base, including 1-(β -methoxyethyl)piperazine. Preparation of monosubstituted piperazines is attended with difficulties, 1-ethoxycarbonylpiperazine being generally employed as an intermediate. The reported facile hydrogenolysis of benzylpiperazines (Birkofer 1942; Baltzly and Russell 1954) makes a simple preparation of this intermediate desirable.

Baltzly *et al.* (1944) prepared 1-benzylpiperazine by prolonged reaction (20–80 hr) of piperazine and benzyl chloride, followed by separation of the mono- and dibenzyl compounds. We found that reaction of 1-piperazinium chloride (1 mol) with benzyl chloride almost immediately precipitated 1,4-piperazinium dichloride (0.5 mol), leaving in solution 1-benzyl-4-piperazinium chloride (0.5 mol). No 1,4-dibenzyl compound was found, and the reaction thus appears to follow equation (1).



Alkylation of 1-benzylpiperazine with β -methoxyethyl toluene-*p*-sulphonate gave 1-benzyl-4-(β -methoxyethyl)piperazine. Attempted debenzylation by means of sodium or potassium in liquid ammonia failed, but palladium-charcoal, though unsuccessful in ethanol, effected debenzylation in acetic acid, giving

1-(β -methoxyethyl)piperazine. This could not be prepared by methylation of 1-benzoyl-4-(β -hydroxyethyl)piperazine using either diazomethane or dimethyl sulphate.

1-Benzoylpiperazine has been prepared by Moore, Boyle, and Thorn (1929) in 22 per cent. yield, and by Jacobi (1933) in 51–68 per cent. yield, its isolation involving a series of evaporations and extractions. Moore, Boyle, and Thorn (1929) and Jacobi (1933) reported the optimum pH for this reaction to be *c.* 4 and 3 respectively. However, while Jacobi worked at not less than 50 °C (bath at 80 °C) and in 50 per cent. aqueous acetone, Moore, Boyle, and Thorn used a two-phase reaction system at room temperature.

The ionization constants of piperazine (Kolthoff 1925), pK_{a1} 9.9 and pK_{a2} 5.6 at 15 °C, show the base-weakening effect of the mono-cation on the other nitrogen atom to be greater than that exerted by the benzoyl group in 1-benzoylpiperazine, for which we have found pK_a 7.8 at 20 °C and 7.1 at 50 °C. A pH below 5.8 (in water at 20 °C) is thus required to avoid dibenzoylation of 1-benzoylpiperazine; but since at a pH of 3.6, piperazine would exist wholly as the non-reacting di-cation, the optimum pH for monobenzoylation should be *c.* 4.5–5.5.

The presence of non-aqueous solvents represses ionization; thus 50 per cent. aqueous acetone changes the pK_a of benzoic acid by *c.* 1.5 units from its value in water at 20 °C (Cavill, Gibson, and Nyholm 1949). The difference between the optimum pH found by Moore, Boyle, and Thorn (1929) and Jacobi (1933) may thus be due to the lowering of the pK_a of 1-benzoylpiperazine by the combined effect of change in temperature and solvent.

In our hands monobenzoylation of piperazine in 50 per cent. aqueous acetone proceeded rapidly at a pH of *c.* 4.5, a simplified method of isolation giving 76 per cent. of 1-benzoylpiperazine. None of the disubstituted derivative was found.

II. EXPERIMENTAL

Analyses are by Miss B. Stevenson, University of Sydney, and Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory.

(a) *1-Methoxyphenothiazine*.—A mixture of 2-methoxydiphenylamine (5 g; 0.025 mol), redistilled sulphur (1.6 g; 0.05 mol), and iodine (0.2 g) was heated at 150–160 °C for 45 min and then at 175 °C for 15 min. Distillation gave *1-methoxyphenothiazine* (3.7 g, 65% yield), b.p. 140–160 °C/0.05 mm, which solidified and crystallized from isopropanol as pale yellow needles, m.p. 98.5 °C (Found: C, 67.7; H, 4.7%. Calc. for $C_{13}H_{11}ONS$: C, 68.1; H, 4.9%).

(b) *1-Ethoxyphenothiazine*.—Application of the method used in Section II (a) to 2-ethoxydiphenylamine (8.23 g, n_D^{20} 1.6267) gave *1-ethoxyphenothiazine* (7.2 g, 77% yield), fawn needles from isopropanol, m.p. 81 °C. Sublimation at 80 °C/0.05 mm gave white needles, m.p. 81.5 °C (Found: C, 69.1; H, 5.2%. Calc. for $C_{14}H_{13}ONS$: C, 69.1; H, 5.4%).

(c) *3-Methoxydiphenylamine*.—Decarboxylation of 3'-methoxydiphenylamine-2-carboxylic acid (12.2 g; 0.05 mol; Ullmann and Kipper 1907) at 250–260 °C for 2.5 hr gave *3-methoxydiphenylamine* (8.4 g, 82% yield), b.p. 136–138 °C/0.07 mm, crystallizing from *n*-hexane as white needles, m.p. 72 °C (Found: C, 78.1; H, 6.5%. Calc. for $C_{13}H_{13}ON$: C, 78.3; H, 6.6%).

(d) *Fusion of 3-Methoxydiphenylamine with Sulphur*.—Application of the method used in Section II (a) to 3-methoxydiphenylamine (8 g) gave an oil (4.4 g, 48% yield), b.p.

194–198 °C/0.05 mm, which slowly solidified. Chromatography on alumina of the portion soluble in boiling *n*-hexane afforded 4-methoxyphenothiazine (0.4 g) as colourless needles, m.p. 98 °C (Found: C, 68.5; H, 5.3; O, 6.9%. Calc. for $C_{12}H_{11}ONS$: C, 68.1; H, 4.9; O, 7.0%). The hexane-insoluble portion (3.95 g), crystallized from benzene and sublimed *in vacuo*, gave white plates (2.0 g) of 2-methoxyphenothiazine, m.p. 184.5 °C (Found: C, 67.8; H, 4.9%). Charpentier *et al.* (1952) give m.p. 179–180 °C.

(e) *Fusion of 3-Chlorodiphenylamine with Sulphur.*—Application of the method used in Section II (a) to 3-chlorodiphenylamine (10.2 g, n_D^{27} 1.6218; Ullmann and Tedesco 1907) gave an oil (5.2 g, 44% yield), b.p. 200–206 °C/0.1 mm which solidified. Fractional crystallization from benzene-light petroleum (b.p. 60–90 °C) gave two isomers. The more soluble was 4-chlorophenothiazine (0.7 g, 6% yield), colourless plates from light petroleum (b.p. 60–90 °C), m.p. 111 °C (Found: C, 62.0; H, 3.5; S, 14.2%. Calc. for $C_{12}H_8NSCl$: C, 61.7; H, 3.5; S, 13.8%). The less soluble isomer crystallized from benzene as yellow plates, m.p. 199.5 °C (3.2 g) of 2-chlorophenothiazine (Found: C, 61.7; H, 3.7%). Charpentier *et al.* (1952) give m.p.'s 116 °C and 196–197 °C respectively for 4- and 2-chlorophenothiazine, obtained in unstated yield.

(f) *Fusion of 3-Chloro-4'-methoxydiphenylamine with Sulphur.*—The method used in Section II (a) was applied to 3-chloro-4'-methoxydiphenylamine (18.5 g; King, King, and Muir 1946) and the reaction mixture extracted with boiling benzene (250 ml) and filtered hot. Treatment of the filtrate with light petroleum (b.p. 60–90 °C) gave a solid (11 g, 50% yield), m.p. 160–165 °C, which on chromatography on alumina in benzene solution or on sublimation (160 °C/0.1 mm) gave yellow plates of 2-chloro-7-methoxyphenothiazine, m.p. 175.5 °C (Found: C, 58.9; H, 3.9%. Calc. for $C_{12}H_9ONS$: C, 59.2; H, 3.8%).

The oil left on evaporation of the original benzene-light petroleum filtrate crystallized from light petroleum (b.p. 40–70 °C) as needles, m.p. 118 °C, of 4-chloro-7-methoxyphenothiazine (Found: C, 59.0; H, 4.0%).

(g) *Phenothiazone.*—Phenothiazone (Olivier and Combé 1950), purified by sublimation at 150–155 °C/0.05 mm, had m.p. 162–163 °C. Recrystallization from water or ethanol proved unsatisfactory.

(h) *3-Hydroxyphenothiazine.*—3-Hydroxyphenothiazine (DeEds and Thomas 1942), rapidly filtered under nitrogen, formed colourless plates (70% yield), m.p. 182 °C. Sublimation at 160 °C/0.1 mm gave a sample, m.p. 184 °C (Found: C, 67.2; H, 4.4%. Calc. for $C_{12}H_9ONS$: C, 66.8; H, 4.2%). Harpur, Swales, and Denstedt (1950) give m.p. 179–183 °C; DeEds and Thomas (1942) give m.p. 172–173 °C.

(i) *3-Acetoxyphenothiazine.*—A solution of anhydrous potassium carbonate (10 g; 0.07 mol) in water (200 ml) was added to pure phenothiazone (0.71 g; 0.0033 mol) in pyridine (100 ml), powdered sodium hydrosulphite slowly added to the boiling mixture until the solution was decolorized (10 min), and the cooled mixture then treated gradually with acetic anhydride (7 g; 0.07 mol) with vigorous stirring. 3-Acetoxyphenothiazine separated (0.5 g, 55% yield) and crystallized from benzene as white needles, m.p. 197.5 °C (Found: C, 65.5; H, 4.2%. Calc. for $C_{14}H_{11}O_2NS$: C, 65.3; H, 4.3%). Its decomposition is accelerated by alumina or charcoal.

(j) *3-Ethoxyphenothiazine.*—Prepared from 4-ethoxydiphenylamine as described in Section II (a), but at 155 °C for 80 min, 3-ethoxyphenothiazine (43% yield) crystallized from benzene as yellow plates, m.p. 149 °C (Found: C, 69.2; H, 5.4%).

(k) *3',5'-Dichlorodiphenylamine-2-carboxylic Acid.*—Prepared by the method of Kshatriya, Patel, and Nargund (1946) but using 150–160 °C for 8 hr, the acid (60% yield) crystallized from ethyl acetate as pale yellow needles, m.p. 199.5 °C (Found: C, 55.4; H, 3.3%. Calc. for $C_{12}H_6O_2NCl_2$: C, 55.3; H, 3.2%). Kshatriya, Patel, and Nargund (1946) give m.p. 189–190 °C, 47% yield.

(l) *Fusion of 3',5'-Dichlorodiphenylamine-2-carboxylic Acid with Sulphur.*—Reaction of the preceding dichlorodiphenylaminocarboxylic acid (4.15 g) was carried out as described in Section

II (a) but at 180–190 °C for 1.5 hr. The reaction mixture was refluxed with light petroleum (b.p. 60–90 °C) and filtered. The insoluble residue was washed with saturated sodium bicarbonate solution and crystallized from benzene as yellow plates, m.p. 287.5 °C, of 2,8-dichlorophenothiazine (1.2 g, 30% yield) (Found: C, 53.8; H, 2.6%. Calc. for $C_{11}H_7NCl_2S$: C, 53.7; H, 2.6%).

The light petroleum solution was washed with sodium bicarbonate solution and passed through a column of alumina giving 2,6-dichlorophenothiazine (0.35 g, 9% yield) as yellow plates, m.p. 139.5 °C, unchanged on crystallization from light petroleum (b.p. 60–90 °C) (Found: C, 53.9; H, 2.8%).

(m) 1,2,3,4-Tetrahydroquinoxaline.—A mixture of lithium aluminium hydride (3 g), 2,3-dihydroxyquinoxaline (4.85 g; Newbold and Spring 1948) and *N*-ethylmorpholine (100 g) was refluxed for 3 hr at 70 °C under reduced pressure (14 mm). After removal of solvent *in vacuo*, the residue was treated with saturated ammonium chloride solution, refluxed for 15 min, and filtered. On cooling, unchanged starting-material separated (0.8 g) and was removed. The filtrate was basified at 0 °C and extracted with ether.

The solid residue from the original filtration was extracted with boiling ethanol until no more base was taken up; the solvent was removed and the residue partitioned between sodium hydroxide solution and ether.

The combined ethereal extracts afforded 1,2,3,4-tetrahydroquinoxaline (0.95 g, 28% yield) as microcrystals, m.p. 91–95 °C, from benzene-light petroleum (b.p. 60–90 °C) undepressed with an authentic specimen (m.p. 95 °C). Sublimation at 90 °C/0.1 mm gave plates, m.p. 96 °C. The tartrate crystallized from ethanol as white needles, m.p. 150 °C (Found: C, 50.6; H, 5.6%. Calc. for $C_8H_{10}N_2C_4H_8O_6$: C, 50.7; H, 5.7%).

(n) 1,4-Benzoxazin-2-one.—A boiling solution of 2-nitrophenoxyacetic acid (37.2 g; Jacobs and Heidelberg 1917) in water (1 l), containing sodium hydroxide (16 g) was treated gradually with sodium hydrosulphite dihydrate until decolorized. After a further 30 min heating, the solution was acidified to Congo red, boiled to coagulate sulphur, and filtered hot. On cooling, 1,4-benzoxazin-2-one separated as white plates (18.7 g, 66% yield), m.p. 171.5 °C. Jacobs and Heidelberg (1917) give m.p. 173–173.5 °C (corr.).

(o) 2,3-Dihydro-1,4-benzoxazin.—A mixture of 1,4-benzoxazin-2-one (4.25 g), lithium aluminium hydride (1.65 g), and ether (550 ml) was refluxed for 12 hr. Addition of saturated ammonium chloride solution, solid sodium hydroxide, and extraction with ether gave 2,3-dihydro-1,4-benzoxazin (2.95 g, 77% yield) as an oil, b.p. 86–88 °C/0.5 mm, n_D^{21} 1.5975. Knorr (1889) gives b.p. 268 °C/760 mm.

The hydrochloride separated from ethanol-ether as white needles, m.p. 137 °C (Found: C, 55.9; H, 5.9%. Calc. for $C_8H_9ON.HCl$: C, 56.0; H, 5.9%). Knorr (1889) gives m.p. 120 °C. The picrate (from ethanol) had m.p. 155 °C (Found: C, 46.2; H, 3.4%. Calc. for $C_8H_9ON.C_6H_3O_7N_3$: C, 46.1; H, 3.3%).

(p) Morpholine Acetate.—This salt crystallized from ethanol-ether as needles, m.p. 112 °C (Found: C, 48.5; H, 9.1%. Calc. for $C_4H_9ON.C_2H_3O_2$: C, 48.9; H, 8.9%).

(q) 1,4-Thiazane.—A solution of 2,2'-dichlorodiethylamine hydrochloride (17.85 g; 0.1 mol; prepared in 94% yield from 2,2'-dihydroxydiethylamine by an adaptation of Raiziss and Clemence's (1941) method) in 95% ethanol (100 ml) was treated gradually with a solution of sodium sulphide nonahydrate (42 g; 0.175 mol) in hot 95% ethanol (500 ml). A transient red colour soon disappeared and sodium chloride separated. After refluxing for 1 hr, the cold solution was filtered and the sodium chloride (15 g, 86% of theory) was washed (ethanol). The filtrate was acidified to litmus with alcoholic hydrogen chloride and refluxed for 30 min. Removal of solvent to a bulk of 50 ml, and addition of water (150 ml) and sodium hydroxide caused separation of an oily layer which was separated and the solution extracted with chloroform. Distillation of the combined upper layer and extracts gave 1,4-thiazane (5.85 g, 66% yield), b.p. 174 °C/763 mm, n_D^{14} 1.5382. Sommers and Horrom (1954) and Davies (1920) give b.p.'s 168–170 °C and 174 °C/746 mm and n_D^{20} 1.5386. The acetate crystallized from ethanol-ether

as white needles, m.p. 149 °C (Found : C, 44.3; H, 7.9%. Calc. for $C_6H_9NS.C_2H_4O_2$: C, 44.2; H, 8.0%). It sublimed at 60 °C/0.1 mm.* The picrate had m.p. 200 °C (Found : C, 36.1; H, 3.5%. Calc. for $C_6H_9NS.C_6H_3O_7N_3$: C, 36.1; H, 3.6%). Sommers and Horrom (1954) and Davies (1920) report m.p. 198 °C and 204–205 °C respectively.

(r) *1-Ethoxycarbonylpiperazine Tartrate*.—This salt crystallized from 95% ethanol as colourless plates, m.p. 139–140 °C (Found : C, 42.5; H, 6.4%. Calc. for $C_7H_{14}O_2N_2.C_4H_4O_6$: C, 42.7; H, 6.5%).

(s) *1,4-Dimethylpiperazine Diacetate*.—This salt formed a stable hemihydrate, b.p. 48–50 °C/0.5 mm, n_D^{20} 1.4414 (Found : C, 49.4; H, 9.2%. Calc. for $C_8H_{14}N_2.2C_2H_3O_2.0.5H_2O$: C, 49.4; H, 9.4%).

(t) *1-Benzylpiperazine*.—A mixture of piperazine hexahydrate (48.5 g; 0.25 mol), ethanol (100 ml), and ethanolic hydrogen chloride (25 ml of 8.4N; 0.21 mol) at 40 °C was treated with benzyl chloride (31.6 g; 0.25 mol) over 10 min with vigorous stirring. Precipitation of colourless needles began immediately and ceased after 15 min. Filtration gave 1,4-piperazinium dichloride monohydrate (18.2 g, 0.103 mol, 82.5% of theory), subliming at 295–315 °C (Found : equiv., 89.1. Calc. for $C_7H_{10}N_2.2HCl.H_2O$: equiv., 88.5).

To the filtrate was added a further 25 ml ethanolic hydrogen chloride (8.4N) and dry ether until precipitation was complete. Colourless plates of 1-benzylpiperazinium dichloride, m.p. 254 °C (sintering) separated. Baltzly *et al.* (1944) give m.p. 253 °C. The base (17.35 g, 0.99 mol; 79% yield) had b.p. 87–93 °C/0.4 mm, n_D^{20} 1.5473.

(u) *1,4-Di-(β-methoxyethyl)piperazine*.—A vigorous exothermic reaction with liberation of carbon dioxide followed on mixing anhydrous piperazine (2.38 g; 0.028 mol), β-methoxyethyl toluene-*p*-sulphonate (13.8 g; 0.06 mol), and anhydrous potassium carbonate (4.15 g; 0.03 mol). The mixture was heated at 100 °C for 3 hr, water (10 ml) was then added, the pH brought to 2, and the mixture extracted with ether. The aqueous layer was basified and extracted with chloroform. Distillation of the chloroform extracts gave 1,4-di-(β-methoxyethyl)piperazine as an oil, b.p. 62–66 °C/0.1 mm, n_D^{25} 1.4650. The *dipicrate* crystallized from acetone as needles, m.p. 234.5 °C (Found : C, 39.8; H, 4.2%. Calc. for $C_{10}H_{22}O_2N_2.2C_6H_3O_7N_3$: C, 40.0; H, 4.3%), and the *dihydrochloride* separated from ethanol-ethyl acetate as needles of a monohydrate, m.p. 84 °C, resolidifying and remelting at 223.5 °C (Found : C, 41.4; H, 9.0%. Calc. for $C_{10}H_{22}O_2N_2.2HCl.H_2O$: C, 41.1; H, 8.9%).

(v) *1-Benzoyl-4-(β-hydroxyethyl)piperazine*.—Ethylene oxide (5 g) was passed into 1-benzoylpiperazine (9.5 g) in ethanol (50 ml) over 45 min. Distillation gave 1-benzoyl-4-(β-hydroxyethyl)piperazine as a colourless viscous oil (10.25 g, 87% yield), b.p. 162–164 °C/0.1 mm.

The *hydrochloride* crystallized from ethanol as needles, m.p. 210.5 °C (Found : C, 57.5; H, 6.9%. Calc. for $C_{15}H_{18}O_2N_2.HCl$: C, 57.6; H, 7.1%) and the *picrate* formed yellow needles from aqueous ethanol, m.p. 194.5 °C (Found : C, 49.3; H, 4.7%. Calc. for $C_{15}H_{18}O_2N_2.C_6H_3O_7N_3$: C, 49.2; H, 4.6%).

(w) *1-Benzyl-4-(β-methoxyethyl)piperazine*.—Reaction of 1-benzylpiperazine (8.8 g; 0.05 mol), β-methoxyethyl toluene-*p*-sulphonate (12.65 g; 0.055 mol), and anhydrous potassium carbonate (6.9 g; 0.05 mol) was exothermic, cooling being required to maintain the temperature at 100 °C. The mixture solidified; after a further 30 min at 100 °C, water (30 ml) was added with warming until solution was complete, when hydrochloric acid (10N) was added to Congo red and the solution extracted with ether. The aqueous layer was basified at 0 °C and extracted with ether and chloroform. Distillation of the combined extracts gave 1-benzyl-4-(β-methoxyethyl)piperazine (9.74 g, 83% yield) as a colourless oil, b.p. 124–125 °C/0.3 mm, $n_D^{14.5}$ 1.5242 (Found : C, 71.6; H, 9.4%. Calc. for $C_{14}H_{22}ON_2$: C, 71.7; H, 9.5%). The *dihydrochloride* formed needles from ethanol, m.p. 236 °C (Found : C, 54.5; H, 7.7%. Calc. for $C_{14}H_{22}ON_2.2HCl$: C, 54.7; H, 7.9%).

The *dipicrate* crystallized from water as yellow needles, m.p. 240 °C (decomp.) (Found : C, 44.8; H, 4.1%. Calc. for $C_{14}H_{22}ON_2.2C_6H_3O_7N_3$: C, 45.1; H, 4.1%).

(x) 1-(β -Methoxyethyl)piperazine.—A solution of 1-benzyl-4-(β -methoxyethyl)piperazine (2.35 g; 0.01 mol) in acetic acid (25 ml) was shaken with hydrogen and palladium-charcoal catalyst (2 g; 10%) until absorption ceased (1 hr). After filtration and removal of solvent *in vacuo*, the residue was basified and extracted with chloroform. Distillation gave 1-(β -methoxyethyl)piperazine as a colourless oil (0.65 g, 45% yield), b.p. 40–41 °C/0.3 mm, n_D^{14} 1.4743 (Found: C, 57.7; H, 11.3%. Calc. for $C_7H_{16}ON_2$: C, 58.3; H, 11.2%). The dihydrochloride crystallized from ethanol-ether as white needles, m.p. 213 °C containing water of crystallization (Found: C, 37.9; H, 8.2%. Calc. for $C_7H_{16}ON_2 \cdot 2HCl \cdot 0.25H_2O$: C, 37.9; H, 8.4%) and the dipicrate formed yellow plates, m.p. 227 °C, from water (Found: C, 38.1; H, 3.8%. Calc. for $C_7H_{16}ON_2 \cdot 2C_6H_3O_7N_3$: C, 37.9; H, 3.7%).

(y) 1-Benzoylpiperazine.—A solution of piperazine hexahydrate (3.9 g; 0.02 mol) in water (80 ml) was treated with bromocresol green indicator (6 drops of 0.04% soln.) and hydrochloric acid (c. 4 ml of 10N) until the colour of the solution was bluish-green (pH c. 4.5). Acetone (100 ml) was added, followed by benzoyl chloride (5.62 g; 0.04 mol), and a solution of potassium hydroxide (4.5 g; 0.08 mol) in water (20 ml) was then added dropwise with rapid stirring over 15 min keeping the colour of the solution green, but not allowing it to become either blue or yellow. After this time the solution no longer showed any tendency to become acidic.

Acetone was distilled off and the residual solution acidified to pH 2 by addition of hydrochloric acid (10N) and cooled to 0 °C. Filtration of the precipitate gave benzoic acid (2.55 g, 0.021 mol), m.p. and mixed m.p. 121 °C. The filtrate was basified with potassium carbonate and extracted exhaustively with chloroform. Distillation of the extracts gave 1-benzoylpiperazine (2.9 g, 0.015 mol, 76% yield), b.p. 142–146 °C/1 mm, m.p. 74–75 °C. Jacobi (1933) gives m.p. 75 °C. Potentiometric titration of an aqueous solution with 0.1N hydrochloric acid at 20 °C gave pK_a 7.8, and at 50 °C gave pK_a 7.1.

III. ACKNOWLEDGMENTS

The authors wish to thank Mr. D. Ford and Messrs. Timbrol Ltd. for the measurements of the infra-red spectra. This work was associated with the research programme of the McMaster Animal Health Laboratory, Division of Animal Health and Production, C.S.I.R.O., which one of us (M.E.T.) thanks for arranging a research grant from the Ian McMaster Bequest.

IV. REFERENCES

- BALTZLY, R., BUCK, J. S., LORZ, E., and SCHON, W. (1944).—*J. Amer. Chem. Soc.* **66**: 263.
 BALTZLY, R., and RUSSELL, P. B. (1954).—*J. Amer. Chem. Soc.* **76**: 5776.
 BIRKOFER, L. (1942).—*Ber. dtsh. chem. Ges.* **75**: 429.
 CAVILL, G. W. K., GIBSON, N. A., and NYHOLM, R. S. (1949).—*J. Chem. Soc.* **1949**: 2466.
 CHARPENTIER, P., GAILLOT, P., JACOB, R., GAUDECHON, J., and BUISSON, P. (1952).—*C.R. Acad. Sci. Paris* **235**: 59.
 CRAGOE, E. J., and HAMILTON, C. S. (1945).—*J. Amer. Chem. Soc.* **67**: 536.
 CYMERMAN-CRAIG, J., ROGERS, W. P., and WARWICK, G. P. (1955).—*Aust. J. Chem.* **8**: 252.
 DAVIES, W. (1920).—*J. Chem. Soc.* **117**: 297.
 DEEDS, F., and THOMAS, J. O. (1942).—*J. Parasitol.* **28**: 363.
 HARPUR, R. P., SWALES, W. E., and DENSTEDT, O. F. (1950).—*Canad. J. Res. D* **28**: 143.
 HOUSTON, D. F., KESTER, E. B., and DEEDS, F. J. (1949).—*J. Amer. Chem. Soc.* **71**: 3819.
 IDSON, B., and SPOERRI, P. E. (1954).—*J. Amer. Chem. Soc.* **76**: 2902.
 JACOBI, K. R. (1933).—*Ber. dtsh. chem. Ges.* **66**: 113.
 JACOBS, W. A., and HEIDELBERGER, M. (1917).—*J. Amer. Chem. Soc.* **39**: 2188.
 KSHATRIYA, K. C., PATEL, S. R., and NARGUND, K. S. (1946).—*J. Univ. Bombay A* **15**: 42. (*Chem. Abstr.* **41**: 6214.)
 KING, F. E., KING, T. J., and MUIR, I. H. M. (1946).—*J. Chem. Soc.* **1946**: 5.
 KNOBB, L. (1889).—*Ber. dtsh. chem. Ges.* **22**: 2081.
 KOLTHOFF, J. M. (1925).—*Biochem. Z.* **162**: 300.

- LANGLET, N. A. (1896).—*Bih. Svensk. Vetensk. Handl.* **22** (ii): 3.
- MASSIE, S. P. (1954).—*Chem. Rev.* **54**: 797.
- MOORE, T. S., BOYLE, M., and THORN, V. M. (1929).—*J. Chem. Soc.* **1929**: 39.
- NEWBOLD, G. T., and SPRING, F. S. (1948).—*J. Chem. Soc.* **1948**: 519.
- OLIVIER, S. C. J., and COMBÉ, W. P. (1950).—*Rec. Trav. Chim.* **69**: 526.
- RAIZISS, G. W., and CLEMENCE, L. W. (1941).—*J. Amer. Chem. Soc.* **63**: 3124.
- SMITH, N. L. (1950).—*J. Org. Chem.* **15**: 1125.
- SOMMERS, A. H., and HORROM, B. W. (1954).—*J. Amer. Chem. Soc.* **76**: 1187.
- ULLMANN, F., and KIPPER, H. (1907).—*Liebigs Ann.* **355**: 342.
- ULLMANN, F., and TEDESCO, E. (1907).—*Liebigs Ann.* **355**: 337.

TRITERPENOID COMPOUNDS*

II. SOME DEHYDRATIONS OF 3 β -HYDROXYTRITERPENOIDS

By A. B. BURNS,[†] A. R. H. COLE,[†] B. J. PARKES,[†] and D. E. WHITE[†]

[Manuscript received February 15, 1956]

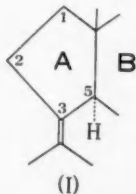
Summary

Dehydrations of methyl 3 β -hydroxylupan-28-oate (methyl dihydrobetulate) and methyl 3 β -hydroxyurs-12-en-28-oate (methyl ursolate) have been carried out by several different procedures and the constitutions of the crystalline products established. The reactions of β -amyirin methanesulphonate have been re-examined but no product corresponding to α -amyradiene-IV (Noller and Hearst 1950) was obtained crystalline.

Reduction of methyl ursolate methanesulphonate with lithium aluminium hydride afforded uvaol.

I. INTRODUCTION

A variety of different methods has been employed for the dehydration of 3 β -hydroxytriterpenoids and it has been established that pyrolysis of their benzoates (Jeger *et al.* 1947; Davy, Halsall, and Jones 1951) results in the formation of Δ^2 -unsaturated compounds, while the use of phosphorus pentachloride in light petroleum (Ruzicka *et al.* 1945*a*, 1945*b*, 1945*c*, 1946, 1948*a*, 1948*b*) results in a retopinacoline rearrangement with the formation of 3-*isopropylidene*-A-nor-23,24-bisnor-compounds (I). The latter isomerize in the presence of acid or of palladized calcium carbonate and hydrogen to products with an endocyclic double bond, which are also obtained on dehydration with fuller's earth in boiling xylene (Ruzicka *et al.* 1945*d*, 1946).



We have now obtained methyl lup-2-en-28-oate in good yield by pyrolysis of methyl 3 β -hydroxylupan-28-oate benzoate and confirmed its constitution by observation of the absorption bands at 1661 (CCl_4) and 729 cm^{-1} (CS_2), characteristic of a disubstituted double bond in a 6-membered ring (Henbest,

* The Constitution of A₁-Barrigenol, *Chem. & Ind.* 1955: 254, is regarded as Part I of this series.

[†] Chemistry Department, University of Western Australia, Nedlands, W.A.

Meakins, and Wood 1954). The same compound was also obtained by dehydration of methyl 3 β -hydroxylupan-28-oate with phosphoryl chloride in boiling pyridine and by boiling a pyridine solution of methyl 3 β -hydroxylupan-28-oate methanesulphonate, but the yields were not as good as in the benzoate pyrolysis.

Treatment of methyl 3 β -hydroxylupan-28-oate with phosphorus pentachloride afforded the expected methyl 3-isopropylidene-A-nor-23,24-bisnorlupan-28-oate, identified by treatment with osmium tetroxide and oxidation of the resultant glycol with lead tetra-acetate. This yielded methyl 3-oxo-A-nor-23,24-bisnorlupan-28-oate which showed the characteristic absorption of a 5-membered-ring ketone at 1740 cm^{-1} , together with a methyl ester carbonyl at 1730 cm^{-1} and a band at 1413 cm^{-1} indicative of a methylene group adjacent to the ring carbonyl. The intensity of the latter band (320 units; Bottomley, Cole, and White 1955) indicated that there was only one methylene adjacent to the carbonyl.

Similarly, methyl 3 β -hydroxyurs-12-en-28-oate has been dehydrated to methyl urs-2,12-dien-28-oate by pyrolysis of its benzoate, by treatment with phosphoryl chloride in pyridine, and by heating its methanesulphonate in pyridine. On heating the methanesulphonate in methanol-hydrochloric acid the only crystalline product obtained was a little of the original hydroxy ester, while pyrolysis of the methanesulphonate did not afford any crystalline product.

The compound prepared by Huzii and Osumi (1939) and tentatively formulated (Elsevier 1952) as methyl urs-2,12-dien-28-oate is not identical with our compound of this structure. It is probably methyl 3-isopropylidene-A-nor-23,24-bisnorurs-12-en-28-oate. We are indebted to a referee for drawing our attention to this.

Our results with methyl 3 β -hydroxyurs-12-en-28-oate methanesulphonate contrast with those obtained by Noller and Hearst (1950) with urs-12-en-3 β -yl (α -amyrin) methanesulphonate. We have, therefore, re-examined the reactions of α -amyrin methanesulphonate and confirmed the formation of α -amyradiene-III on pyrolysis. The structure of this compound has now been established (Fayez *et al.* 1955). Although we failed to isolate α -amyradiene-IV, Professor F. S. Spring (personal communication) has informed us that this compound has been obtained and its structure established in his laboratory.

The presence of the 28-methoxycarbonyl group in methyl ursolate apparently inhibits the double bond migration responsible for the formation of α -amyradiene-III and α -amyradiene-IV from α -amyrin.

An attempt to reduce methyl 3 β -hydroxyurs-12-en-28-oate methanesulphonate with lithium aluminium hydride resulted in reduction of the methyl ester group, but in hydrolysis rather than reduction of the methanesulphonate. Similar results have recently been reported by King, Godson, and King (1955) in the diterpene group with the methanesulphonates of the primary alcohols, vinhaticol and vouacapenol. The good yield obtained by Eschenmoser and Frey (1952) in the reduction of 2-methyl-2-hydroxymethylcyclopentanone methanesulphonate to 2,2-dimethylcyclopentanol may be exceptional in view of the presence of a β -keto grouping.

II. EXPERIMENTAL

M.p.'s were determined in evacuated capillaries and are corrected. Microanalyses are by the C.S.I.R.O. Microanalytical Laboratory under the direction of Dr. K. W. Zimmermann.

Infra-red absorption spectra were determined on a Grubb-Parsons S3A instrument, and unless otherwise indicated were in carbon tetrachloride solution.

"Working up in the usual way" with a solvent indicates extraction with that solvent followed by washing with acid, alkali, and water, drying (Na_2SO_4), and evaporating the solvent.

Alumina for chromatography was washed with nitric acid and standardized by the method of Brockmann and Schodder (1941).

Light petroleum refers to the fraction b.p. 60–80 °C.

(a) *Methyl 3 β -Hydroxyluplan-28-oate Benzoate*.—Benzoyl chloride (0.5 ml) was added to a solution of methyl 3 β -hydroxyluplan-28-oate (1.13 g) in dry pyridine (30 ml) and after 2 days, poured into water (1 l.) containing hydrochloric acid (30 ml). The solid product (1.4 g) was washed with boiling water and formed colourless plates of *methyl 3 β -hydroxyluplan-28-oate benzoate*, m.p. 249–250 °C, from methylene chloride-methanol (Found: C, 79.4; H, 9.9%. Calc. for $\text{C}_{33}\text{H}_{54}\text{O}_4$: C, 79.1; H, 9.8%). It depressed the m.p. of a sample of methyl 3 β -hydroxyluplan-20(29)-en-28-oate benzoate (methyl betulate benzoate), m.p. 248–249 °C, by c. 5 °C.

(b) *Methyl 3 β -Hydroxyluplan-28-oate Methanesulphonate*.—Methanesulphonyl chloride (200 mg) in dry pyridine (5 ml) was added slowly to methyl 3 β -hydroxyluplan-28-oate (415 mg) in dry pyridine (10 ml). After 18 hr the product was worked up in the usual way with chloroform and formed colourless needles of *methyl 3 β -hydroxyluplan-28-oate methanesulphonate*, m.p. 119–120 °C (decomp.), from chloroform-methanol (Found: C, 69.3; H, 9.9; O, 15.3%. Calc. for $\text{C}_{33}\text{H}_{54}\text{O}_8$: C, 69.8; H, 9.9; O, 14.5%).

(c) *Methyl Lup-2-en-28-oate*.—(i) Methyl 3 β -hydroxyluplan-28-oate benzoate (243 mg) was heated in a 6 by 1 in. test tube to 350–360 °C for 2 hr in a nitrogen atmosphere. Sublimate was occasionally melted with a free flame and returned to the bottom of the tube. The product was saponified with potassium hydroxide (1 g) in methanol (15 ml) for 5 hr under reflux. Working up in the usual way with chloroform yielded a brown solid (180 mg). After chromatography on alumina (activity III), *methyl lup-2-en-28-oate* (165 mg) was obtained in the light petroleum eluates. It formed thick colourless needles, m.p. 188.5–189 °C, after repeated crystallization from methylene chloride-methanol (Found: C, 82.0; H, 11.0%. Calc. for $\text{C}_{31}\text{H}_{50}\text{O}_2$: C, 81.9; H, 11.1%).

(ii) Freshly distilled phosphoryl chloride (2.5 ml) was added to methyl 3 β -hydroxyluplan-28-oate (500 mg) in dry pyridine (15 ml) and refluxed for 2½ hr. Working up in the usual way with chloroform yielded a brown oil (450 mg) which was chromatographed on alumina (activity II; 5 g). A clear glass (315 mg) was eluted with light petroleum and formed colourless needles (80 mg) of methyl lup-2-en-28-oate, m.p. 187–188.5 °C, from chloroform-methanol. Its m.p. was not depressed by material prepared by method (i) above.

(iii) Methyl 3 β -hydroxyluplan-28-oate methanesulphonate (100 mg) in dry pyridine (10 ml) was refluxed for 3 days. On working up in the usual way with chloroform a dark brown gum was obtained. The fraction of this which dissolved in light petroleum was chromatographed on alumina (activity I; 5 g). The material eluted with light petroleum formed colourless needles (22 mg) of methyl lup-2-en-28-oate, m.p. 187 °C, from methylene chloride-methanol, identical with the products from (i) and (ii) above.

(d) *Methyl 3-isoPropylidene-A-nor-23, 24-bisnorluplan-28-oate*.—Phosphorus pentachloride (1 g) was added to a suspension of methyl 3 β -hydroxyluplan-28-oate (1.05 g) in light petroleum (10 ml) and stirred for 1 hr at room temperature. After pouring onto crushed ice and working up in the usual way with ether, a brown glass was obtained. Chromatography on alumina (activity I) yielded 341 mg in the first light petroleum eluate which formed thick colourless needles (140 mg) of *methyl 3-isoPropylidene-A-nor-23, 24-bisnorluplan-28-oate*, m.p. 143–144 °C, from methanol (Found: C, 81.4; H, 10.9%. Calc. for $\text{C}_{31}\text{H}_{44}\text{O}_2$: C, 82.2; H, 10.7%). The low C value may be due to the presence of a small amount of chloro-compound.

(e) *Methyl 3-Oxo-A-nor-23, 24-bisnorlupan-28-oate*.—A solution of osmium tetroxide (100 mg) in dry ether (15 ml) was added to methyl 3-isopropylidene-A-nor-23, 24-bisnorlupan-28-oate (140 mg) in pyridine (2 ml). After a week in the dark, water (5 ml) was added and after evaporation of the ether, mannitol (300 mg), potassium hydroxide (200 mg), benzene (5 ml), and methanol (10 ml) were added and the solution refluxed for 4 hr. On adding water (50 ml) and working up in the usual way with chloroform, a product (150 mg), m.p. 105–110 °C, was obtained. This was dissolved in acetic acid (10 ml) and lead tetra-acetate (500 mg) added. Next day, water (10 ml) was added and the solvents removed *in vacuo*. The residue was extracted with chloroform and formed colourless needles (22 mg) of *methyl 3-oxo-A-nor-23, 24-bisnorlupan-28-oate*, m.p. 182–182.5 °C, from methanol (Found: C, 78.3; H, 10.1%. Calc. for $C_{32}H_{44}O_8$: C, 78.5; H, 10.3%).

(f) *Methyl 3 β -Hydroxyurs-12-en-28-oate Methanesulphonate*.—To a solution of methyl 3 β -hydroxyurs-12-en-28-oate (1.3 g; dried at 100 °C/18 mm) in dry pyridine (10 ml) cooled to 0 °C methanesulphonyl chloride (0.3 ml) was added dropwise. After 48 hr at 0 °C the product was worked up in the usual way with chloroform and formed colourless needles (1.03 g) of *methyl 3 β -hydroxyurs-12-en-28-oate methanesulphonate*, m.p. 129–130 °C (decomp.), from methylene chloride-methanol (Found: C, 70.3; H, 9.4; S, 6.0%. Calc. for $C_{32}H_{44}O_8S$: C, 70.0; H, 9.6; S, 5.8%). The analytical sample was dried at room temperature and 0.1 mm for a week. Higher temperatures led to some decomposition.

Refluxing in methanolic hydrochloric acid resulted in hydrolysis to methyl 3 β -hydroxyurs-12-en-28-oate but no crystalline product was isolated after pyrolysis at 110 °C for 6 hr, or at 130 °C for 8 min. The methanesulphonate was recovered unchanged after treatment with lithium hydride in boiling ether for 5 hr or in boiling benzene for 2 hr.

(g) *Methyl Ursa-2, 12-dien-28-oate*.—(i) Methyl 3 β -hydroxyurs-12-en-28-oate benzoate (500 mg) was heated to 320–330 °C for 30 min and the resulting brown resin saponified with alc. potassium hydroxide (10%; 50 ml) for 3 hr under reflux. Water (500 ml) was added and the product worked up in the usual way with chloroform and chromatographed on alumina (activity II; 10 g). Light petroleum (200 ml) eluted *methyl ursa-2, 12-dien-28-oate* (80 mg), which formed colourless needles, m.p. 195–196 °C, from chloroform-methanol (Found: C, 82.1; H, 10.4%. Calc. for $C_{31}H_{50}O_2$: C, 81.9; H, 11.1%) and absorbed at 1659 cm^{-1} (double bond stretching) and 729 cm^{-1} (CS_2). Further elution with light petroleum (100 ml) yielded mixtures (30 mg) and then (300 ml) unchanged methyl 3 β -hydroxyurs-12-en-28-oate (200 mg).

(ii) Methyl 3 β -hydroxyurs-12-en-28-oate methanesulphonate (200 mg) in dry pyridine (10 ml) was refluxed for 24 hr and the product isolated by pouring into dilute hydrochloric acid (100 ml). After saponification with methanolic potassium hydroxide (10%) for 25 min and pouring into water, extraction with chloroform yielded a red resin (148 mg). Chromatography on alumina (activity II; 4 g) yielded 60 mg to light petroleum and 20 mg to benzene-light petroleum (1:19). Crystallization from methylene chloride-methanol afforded *methyl ursa-2,12-dien-28-oate* (25 mg) as colourless needles, m.p. 196 °C, undepressed by a sample prepared by method (i) above.

(iii) Phosphoryl chloride (24 ml) was added to a solution of methyl 3 β -hydroxyurs-12-en-28-oate (750 mg) in pyridine (120 ml). Next day, the mixture was poured into water and worked up in the usual way with ether. Chromatography on alumina (activity II; 15 g) yielded 130 mg to benzene-light petroleum (1:9; 350 ml), which formed colourless needles, m.p. 196 °C, from methylene chloride-methanol, identical (m.p. and I.R. absorption) with material prepared by method (i) above.

(h) *Reduction of Methyl 3 β -Hydroxyurs-12-en-28-oate Methanesulphonate with Lithium Aluminium Hydride*.—To methyl 3 β -hydroxyurs-12-en-28-oate methanesulphonate (400 mg) in dry ether, lithium aluminium hydride (130 mg) was added and the mixture refluxed for 5 hr. After adding ethyl acetate, water, and dilute sulphuric acid the product was worked up in the usual way with ether. The residue, after evaporation of the ether and sulphur compounds *in vacuo*, formed long colourless needles (178 mg), m.p. 222–223 °C, from methanol, identical with an authentic sample of urs-12-en-3 β , 28-diol (uvacol) prepared by lithium aluminium hydride reduction

of methyl 3 β -hydroxyurs-12-en-28-oate. A further quantity (84 mg) was isolated from the mother liquors after chromatography on alumina.

(i) *Pyrolysis of Urs-12-en-28-yl Methanesulphonate*.—Urs-12-en-28-yl methanesulphonate (100 mg; m.p. 127°C) was heated at 115°C for 5 min after melting. The product was worked up in the usual way with ether-chloroform (5:1) and chromatographed on alumina (activity II; 2 g). Elution with light petroleum afforded colourless needles (40 mg), m.p. 195°C, from light petroleum.

(j) *Urs-12-en-28-yl Methanesulphonate in Pyridine*.—Urs-12-en-28-yl methanesulphonate (200 mg) in dry pyridine (20 ml) was refluxed for 5 hr and the almost black solution worked up in the usual way with chloroform. The red resin (152 mg) obtained did not crystallize and failed to yield any crystalline fractions after chromatography on alumina.

III. ACKNOWLEDGMENTS

The authors are indebted to the Nuffield Foundation for the provision of the infra-red spectrometer and for a Fellowship (to A.R.H.C.), and to the University Research Fund for financial assistance.

IV. REFERENCES

- BOTTOMLEY, W., COLE, A. R. H., and WHITE, D. E. (1955).—*J. Chem. Soc.* **1955**: 2624.
BROCKMANN, H., and SCHODDER, H. (1941).—*Ber. dtsch. chem. Ges.* **74**: 73.
DAVY, G. S., HALSALL, T. G., and JONES, E. R. H. (1951).—*J. Chem. Soc.* **1951**: 458.
ELSEVIER (1952).—"Elsevier's Encyclopaedia of Organic Chemistry." Vol. 14. Suppl. p. 1099S. (Elsevier: Amsterdam.)
ESCHENMOSER, A., and FREY, A. (1952). *Helv. Chim. Acta* **35**: 1660.
FAYEZ, M. B. E., GRIGOR, J., SPRING, F. S., and STEVENSON, R. (1955).—*J. Chem. Soc.* **1955**: 3378.
HENBEST, H. B., MEAKINS, G. D., and WOOD, G. W. (1954).—*J. Chem. Soc.* **1954**: 800.
HUZII, K., and OSUMI, S. (1939).—*J. Pharm. Soc. Japan* **59**: 660. (*Chem. Abstr.* **34**: 1673 (1940).)
JEGER, O., MONTAVON, M., NOWAK, R., and RUZICKA, L. (1947).—*Helv. Chim. Acta* **30**: 1869.
KING, F. E., GODSON, D. H., and KING, T. J. (1955).—*J. Chem. Soc.* **1955**: 1117.
NOLLER, C. R., and HEARST, P. J. (1950).—*J. Amer. Chem. Soc.* **72**: 625.
RUZICKA, L., JEGER, O., and HUBER, W. (1945c).—*Helv. Chim. Acta* **28**: 942.
RUZICKA, L., JEGER, O., and VOLLI, E. (1945a).—*Helv. Chim. Acta* **28**: 767.
RUZICKA, L., MONTAVON, M., and JEGER, O. (1948a).—*Helv. Chim. Acta* **31**: 818.
RUZICKA, L., NORYMBERSKI, J., and JEGER, O. (1945b).—*Helv. Chim. Acta* **28**: 380.
RUZICKA, L., RUDOWSKI, A., NORYMBERSKI, J., and JEGER, O. (1946).—*Helv. Chim. Acta* **29**: 210.
RUZICKA, L., CZPIFOGEL, S., and JEGER, O. (1948b).—*Helv. Chim. Acta* **31**: 498.
RUZICKA, L., VOLLI, E., and JEGER, O. (1945d).—*Helv. Chim. Acta* **28**: 1628.

SOME NATURALLY OCCURRING DIMETHYLCHROMENES

II. ALLOEVODIONE

By K. D. KIRBY* and M. D. SUTHERLAND†

[Manuscript received April 16, 1956]

Summary

The neutral substance $C_{15}H_{11}O_2(OCH_3)_3$, m.p. 81 °C, isolated from the leaves of *Evodia elleryana* F. Muell. by Jones and Wright (1946) is shown to be 5,6,7-trimethoxy-8-acetyl-2,2-dimethylchromene (alloeodione), an isomer of evodione already known from the same plant.

Various samples from the leaves of *E. elleryana* differ in chromene content. A sample from the leaves of *E. bonwickii* F. Muell. contained no neutral chromenes.

I. INTRODUCTION

Jones and Wright (1946), examining the essential oil of *Evodia elleryana* F. Muell. obtained from Stradbroke I., isolated two substances of molecular formula $C_{16}H_{20}O_2$ with m.p.'s 57 and 82 °C. The former (evodione) has been examined by Wright (1948) and shown to be 5,7,8-trimethoxy-6-acetyl-2,2-dimethylchromene. The latter, a minor product, contained three methoxyl groups and like evodione gave a red colour with concentrated sulphuric acid.

The isolation (Sutherland 1949) of 5-methoxy-7-hydroxy-8-acetyl-2,2-dimethylchromene (alloeodionol) from the leaves of *Medicosma cunninghamii* Hook. f. and the demonstration that the substance, m.p. 107 °C, from the leaves of *E. elleryana*, from Mackay (Jones and Wright 1946), is alloeodionoyl methyl ether suggested that the substance, m.p. 81 °C, would be the 8-acetyl isomer (I) of evodione (alloeodione).

II. alloeVODIONE

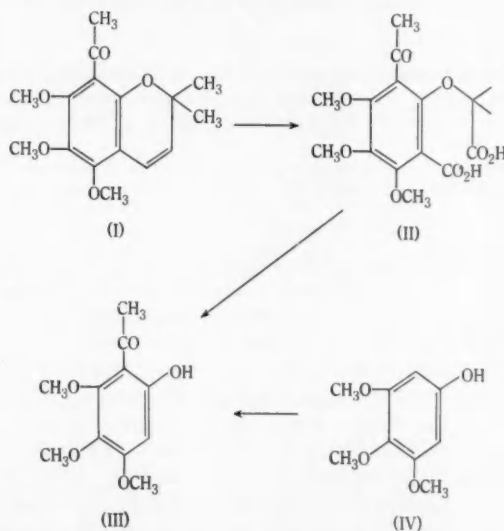
Dried leaves of *E. elleryana* from Atherton were extracted with ether and the residue from the extract was co-distilled with glycerol. The oil from the distillate yielded much crystalline evodione. After this and acidic substances had been separated, the residual oil was distilled into fractions some of which after seeding, deposited more evodione. The mother liquors were chromatographed on alumina to yield in addition to oils, crystalline alloeodione (0.03 per cent. of dry leaf), more evodione (sum total 1.8 per cent. of dry leaf), and alloeodionyl methyl ether (0.008 per cent.) eluted in that order by benzene-light petroleum mixtures.

alloeVodione, m.p. 81 °C, identical with Jones and Wright's (1946) material by mixed melting point, yielded a dinitrophenylhydrazone and a benzylidene

* Imperial Chemical Industries of Australia and New Zealand Ltd., Deer Park, Vic.

† Chemistry Department, University of Queensland.

derivative as oils. The ultraviolet absorption spectrum shows two maxima, λ_{max} 254 m μ , ϵ_{max} 12700; and λ_{max} 322 m μ , ϵ_{max} 3100, with minima at 242 and 304 m μ . Catalytic hydrogenation yielded dihydroalloeodione, m.p. 91–92 °C. The structure of alloeodione was established by the method used previously for evodionol, evodione, and various other substances. alloeodione was oxidized by permanganate in good yield to a dicarboxylic acid (II), pyrolysis of which yielded a yellow oil identified as 2,3,4-trimethoxy-6-hydroxyacetophenone (III) by a mixed melting point test of the dinitrophenylhydrazone, m.p. 173 °C, with a synthetic sample.



The preparation of III as an oil, by the partial methylation of 2,5-dihydroxy-4,6-dimethoxyacetophenone, has been described by Baker (1941). Chapman, Perkin, and Robinson (1927) describe the failure of various methods to bring about the C-acetylation of antiarol (IV), but the present authors found that the not previously attempted Fries's rearrangement of antiaryl acetate gave the required substance III in good yield as an oil, which yielded a crystalline dinitrophenylhydrazone, m.p. 173 °C, and piperonylidene derivative.

III. OCCURRENCE OF DIMETHYLCHROMENES IN PLANTS

The three samples of *E. elleryana*, which have now been examined, show considerable variation in content of evodionol-like chromenes, over and above the effects of different isolation techniques. The identity of the chromenes found, also varies with the sample. This type of variation is known in the alkaloid field (Bick, Ewen, and Todd 1949) and especially in the Australian essential oil field (Penfold 1954), where the varieties distinguished by different oils are known as "physiological forms". A sample from the leaves of

E. bonwickii, examined by the method which we used for *E. elleryana*, was quite free from neutral chromenes. All available data on the occurrence of evodionol-like chromenes in plants have been presented in Table 1. All species listed belong to the family Rutaceae, subfamily Rutoideae.

TABLE 1
DATA ON EVODIONOL-LIKE CHROMENES OCCURRING IN PLANTS

Species	Source	Constituents	Yield (%)	References
<i>Evodia elleryana</i> (leaves)	Queensland Stradbroke I.	Evodione <i>allo</i> Evodione	0.03* 0.001*	Jones and Wright (1946)
<i>E. elleryana</i> .. (leaves)	Mackay	<i>allo</i> Evodionyl methyl ether	0.001*	Jones and Wright (1946)
<i>E. elleryana</i> .. (dry leaves)	Atherton	Evodione <i>allo</i> Evodione <i>allo</i> Evodionyl methyl ether	1.8 0.03 0.008	Present paper
<i>E. bonwickii</i> .. (dry leaves)	Atherton	Neutral chromenes absent	—	
<i>E. vitiflora</i> † .. (leaves)	Springbrook	Evodionol	0.09*	Lahey and Jones (1939); Lahey (1940)
<i>Medicosma cun- ninghamii</i> (dry leaves)	Imbil	<i>allo</i> Evodionol Evodionyl methyl ether Evodionol	0.72 0.18 Trace	Sutherland (1949); present paper
<i>Melicope simplex</i> (bark)	New Zealand	<i>allo</i> Evodionyl methyl ether Evodionol	0.31 0.07	Briggs and Locker (1950)
<i>Acradenia frank- linii</i> (leaves)	Tasmania	<i>allo</i> Evodionyl methyl ether	—	Bick (personal com- munication 1955)

* These yields are undoubtedly too low owing to steam distillation of the leaves as the first step in isolation.

† Described as *E. littoralis* in the references given.

IV. EXPERIMENTAL

(a) *Extraction of Evodia elleryana Leaves.*—Dried *E. elleryana* leaves (18 lb; C.S.I.R.O. SN 4520) from Atherton, north Queensland, were exhausted by ether extraction and the residue from the ether with the addition of a large excess of glycerol was co-distilled from a Claisen flask at less than 1 mm pressure. When the distillate no longer carried oily droplets the total distillate was diluted with water and extracted with ether. Evaporation of the ether, refrigeration of the residue, followed by filtration, and washing with light petroleum yielded 93 g of evodione, m.p.

55–57 °C, not depressed by an authentic sample. The filtrate contained 275 g of a dark viscous oil.

Repeated extraction of the light petroleum-diluted filtrate with 200 ml of 10% NaOH induced the crystallization of a further 27.5 g of evodione.

The passage of CO₂ through the alkaline extract precipitated an oil (c. 50 g) which was separated with ether, evaporated, and distilled *in vacuo*. The distillate (41 g), boiling range 85 °C/1 mm to 180 °C/0.1 mm, was collected in fractions and boiled mainly about 150 °C at 1 mm. The yellow distillate fractions deposited some crystalline material (c. 1 g), which was filtered and crystallized from light petroleum and from methanol to yield colourless waxy crystals, m.p. 61–62 °C, not depressed by admixture with authentic palmitic acid, m.p. 62–63 °C (Found: C, 74.5; H, 12.4%. Calc. for C₁₆H₃₂O₂: C, 75.0; H, 12.5%). The melting point (105–106 °C) of the amide prepared therefrom was not depressed by admixture with authentic palmitamide.

The neutral oil was distilled from a Claisen flask under a gauge pressure of 0.3 mm. To 108 °C, 21 g was obtained; between 108 and 138 °C, 64 g; and from 138 to 155 °C, 84 g. The highest boiling fractions deposited a further 20 g of evodione.

The highest boiling fraction (25 g) was dissolved in light petroleum, chromatographed on an alumina column (10 by 2½ in.), and eluted by light petroleum with a gradually increasing proportion of benzene. The initial fractions (c. 0.9 g) crystallized on seeding with Jones and Wright's (1946) "substance, m.p. 81 °C". Crystallization from light petroleum yielded large monoclinic prisms, m.p. 79.2–80.2 °C (Found: C, 65.9; H, 7.1%. Calc. for C₁₆H₃₀O₃: C, 65.7; H, 6.9%). This substance showed no depression with a sample of Jones and Wright's "substance, m.p. 81 °C", for which the present authors found m.p. 78.5–79.7 °C.

Following fractions yielded more (3.1 g) evodione which gave place in later fractions to *alloevodionyl* methyl ether (0.38 g), m.p. and mixed m.p. 105–106.5 °C. No *evodionyl* methyl ether could be isolated from any fraction.

Numerous oily fractions and a few small isolated crystal crops were also obtained from the chromatogram, but these were not further examined.

(b) *Extraction of E. bonwickii* Leaves.—Dried *E. bonwickii* leaves (10½ lb; C.S.I.R.O. SN5257) from Atherton were treated similarly to the sample described above. The oil (29.9 g) recovered from the glycerol distillate could not be induced to crystallize in spite of seeding with six naturally occurring chromenes. Extraction with 10% NaOH soln. separated 4.6 g of phenols and acids, among which palmitic acid was identified as above. Distillation of the neutral oil gave little material boiling in the evodione range and this could not be induced to crystallize even after chromatography and seeding.

(c) *Hydrogenation of alloeEvodione*.—*alloeEvodione* (57 mg) in ethanol (3 ml), hydrogenated over Adams's catalyst absorbed 4.1 ml of hydrogen (N.T.P.), the calculated volume for 1 mole being 4.37 ml. The solution which was filtered, concentrated, and diluted to cloudiness with water, yielded *dihydroalloeEvodione*, m.p. 91–92 °C, from aqueous ethanol, or light petroleum, (Found: C, 65.7; H, 7.6%. Calc. for C₁₆H₃₂O₃: C, 65.3; H, 7.5%).

(d) *Oxidation of alloeEvodione*.—*alloeEvodione* (0.5 g), dissolved in acetone, was stirred vigorously during 3 hr while potassium permanganate (1.1 g; 50% excess) was added in portions. After a further hour, the manganese dioxide was filtered off, washed thoroughly with acetone, suspended in ice water, and decolourized with sulphur dioxide. The precipitated acid (II, 0.49 g) was extracted with ether and crystallized from water as colourless rhomboids, m.p. 181–182 °C (decomp.) after drying at 100 °C/20 mm for 1 hr (Found: C, 53.8; H, 5.7%; neut. equiv., 177. Calc. for C₁₆H₃₀O₆: C, 53.9; H, 5.6%; neut. equiv. for dibasic acid, 178). From the filtrate was recovered 0.04 g of *alloeEvodione*.

(e) *Pyrolysis of Dibasic Acid (II)*.—The dibasic acid (0.2 g) was treated under water-pump vacuum in a test tube at 185–190 °C for 12 min after which time gas evolution had virtually ceased. The red-brown oily residue was taken up in ether and washed with sodium bicarbonate solution, dried, and recovered as 0.082 g of yellow oil. This substance gave a purple ferric colouration and a chloroform-soluble green copper complex and a 2,4-dinitrophenylhydrazone which

was obtained by Brady's method as dark red prisms, m.p. 173 °C. The mixed melting point with the 2,4-dinitrophenylhydrazone, m.p. 173 °C of 2,3,4-trimethoxy-6-hydroxyacetophenone (see below) was undepressed.

(f) *Fries's Rearrangement of Antiaryl Acetate*.—Anhydrous aluminium chloride (0.67 g) was crushed in nitrobenzene (c. 1 ml) and the suspension poured onto 3,4,5-trimethoxyphenylacetate (0.91 g) in a test tube, which was sealed with a drying tube and heated in an oil-bath at 90 °C until the reactants had melted and had been mixed. The bath temperature was then rapidly raised to 120 °C and further raised to 135 °C during 5 min when frothing ceased. The reaction mixture was cooled, taken up in ice and HCl, and extracted with ether. The ether layer was extracted with 10% NaOH soln. which on acidification yielded to ether, 2,3,4-trimethoxy-6-hydroxyacetophenone (III) as an orange oil (0.69 g) which gave a purple ferric colouration and a chloroform-soluble green copper complex with aqueous copper acetate.

The 2,4-dinitrophenylhydrazone, m.p. 173 °C, was obtained by Brady's method as dark red prisms from ethanol-ethyl acetate (Found: C, 50.4; H, 4.6; OCH₃, 22.8%. Calc. for C₁₄H₈N₄O₈(OCH₃)₃: C, 50.2; H, 4.5; OCH₃, 22.9%).

The piperonylidene derivative was obtained from III and piperonal with 10% NaOH and ethanol by refluxing for $\frac{1}{2}$ hr. After many crystallizations from ethyl acetate and benzene colourless rhomboids, m.p. 183.5–184.5 °C, were obtained (Found: C, 63.8; H, 5.1%. Calc. for C₁₉H₁₈O₇: C, 63.7; H, 5.0%).

V. ACKNOWLEDGMENTS

The authors wish to thank Mr. J. B. Davenport, Division of Food Preservation and Transport, C.S.I.R.O., for a sample of pure palmitic acid; Research Professor F. N. Lahey, University of Queensland, for several combustions and a sample of antiarol; and the Queensland Department of Forestry and Mr. L. J. Webb, Division of Plant Industry, C.S.I.R.O., for supplies of plant material.

VI. REFERENCES

- BAKER, W. (1941).—*J. Chem. Soc.* **1941**: 662.
BICK, I. R. C., EWEN, E. S., and TODD, A. R. (1949).—*J. Chem. Soc.* **1949**: 2767.
BRIGGS, L. H., and LOCKER, R. H. (1950).—*J. Chem. Soc.* **1950**: 2376.
CHAPMAN, E., PERKIN, A. G., and ROBINSON, R. (1927).—*J. Chem. Soc.* **1927**: 3032.
JONES, T. G. H., and WRIGHT, S. E. (1946).—*Pap. Dep. Chem. Univ. Qd.* **1**: No. 27.
LAHEY, F. N. (1940).—*Pap. Dep. Chem. Univ. Qd.* **1**: No. 17.
LAHEY, F. N., and JONES, T. G. H. (1939).—*Pap. Dep. Chem. Univ. Qd.* **1**: No. 13.
PENFOLD, A. R. (1954).—*Perfum. Essent. Oil Rec.* **45**: 213.
SUTHERLAND, M. D. (1949).—*Pap. Dep. Chem. Univ. Qd.* **1**: No. 35.
WRIGHT, S. E. (1948).—*J. Chem. Soc.* **1948**: 2005.

STUDIES IN THE NATURAL COATING OF APPLES

III. SATURATED ACIDS OF THE CUTICLE OIL

By J. B. DAVENPORT*

[*Manuscript received December 15, 1955*]

Summary

The saturated acids, comprising 10.3 per cent. of the cuticle oil of ripe Granny Smith apples, consist principally of stearic and arachidic acids, with smaller amounts of palmitic acid, behenic acid, and acids of higher molecular weight than behenic acid.

I. INTRODUCTION

Parts I and II of this series (Huelin and Gallop 1951*a*, 1951*b*) described four fractions: oil, wax, ursolic acid, and "cutin" occurring in the natural coating of Granny Smith apples, and discussed the changes in these fractions during storage. Particular interest lies in the oil fraction, as, during storage, it increases to 3-4 times its original concentration on the fresh fruit. Accompanying this increase in the oil fraction, there is an increase in the resistance of the skin to gaseous diffusion (Hackney 1943). This latter effect is important in fruit storage and hence a detailed chemical investigation of the oil has been undertaken. The present paper describes the first part of that investigation.

The oil was extracted from mature apples which had been stored at 20 °C for 6 weeks to develop maximum oil content. The saturated acids were separated by low temperature crystallization of the total acids and freed from hydroxy acids by passing the methyl esters through a column of silica gel. The esters were then separated by fractional distillation. The details of this distillation are summarized in Table 1. Mineral oil (predistilled in the fractionating equipment) of appropriate b.p. range was added to the esters in order to amplify the higher boiling components and act as a chaser.

Stearic, arachidic, and behenic acids were isolated from fractions 5, 16, and 24 respectively and identified by mixed m.p. with authentic specimens. Palmitic acid was identified as its hydroxamic acid separated by partition chromatography from material of the first fraction (Davenport 1955), although the boiling point was higher than that of methyl palmitate, being a binary mixture of methyl palmitate and methyl stearate. In order to check whether odd numbered or branched chain acids were present a fraction (11), intermediate in boiling point between methyl stearate and methyl arachidate, was converted to hydroxamic acids and chromatographed; the fraction proved to be a binary mixture of the two esters. The melting point and the acid value of the acids isolated from the pot residue indicated that they were a mixture of higher fatty

* Division of Food Preservation and Transport, C.S.I.R.O., Homebush, N.S.W.

acids, principally tetracosanoic acid. The following approximate percentages of acids present were calculated from the boiling points of the various fractions and expressed as percentages (by weight) of the total saturated acids: palmitic 4, stearic 45, arachidic 39, behenic 6, acids of higher molecular weight than behenic 7.

TABLE I
DISTILLATION DATA

Fraction No.	Boiling Point (°C/1 mm)*	Wt. of Fraction (g)	Isolated Acids	
			Weight (g)	Melting Point† (°C)
1	148.2-151.6	0.60	0.55‡	
2	151.6-154.7	0.64	0.42	64.3-67.3
3	154.7-156.9	0.61	0.34	64.2-66.5
4	156.9-157.3	0.76	0.48‡	
5	157.3	0.69	0.51	62.7-65.3
6	157.3-158.6	0.75	0.35	63.9-65.7
7	158.6-160.1	0.66	0.28	63.0-65.2
8	160.1-161.5	0.74	0.29	62.1-63.9
9	161.5-163.1	0.87	0.29	62.6-63.7
10	163.1-164.2	0.72	0.17	61.2-63.6
11	164.2-164.8	0.86	0.26	64.0-64.6
12	164.8-167.6	1.62	0.51	63.2-66.7
13	167.6-169.6	1.61	1.09	70.4-72.8
14	169.6-171.3	1.54	Lost	
15	171.3-173.5	2.04	0.48	70.6-73.7
16	173.5-174.8	2.14	0.52	71.7-73.9
17	174.8-176.0	1.87	0.33	70.0-73.2
18	176.0-177.6	2.40	0.46	70.0-71.0
19	177.6-180.1	1.80	0.26	69.5-70.0
20	180.1-181.0	1.84	0.25	70.5-71.2
21	181.0-182.2	1.91	0.22	71.0-72.7
22	182.2-183.6	1.97	0.10	74.0-76.4
23	183.6-184.7	1.84	0.04	76.3-77.9
24	184.7-187.0	2.15	0.09	78.6-79.6
25	187.0-188.2	1.88	0.02	75.6-77.2
26	188.2-189.6	1.91	0.02	77.6-78.6
27		2.90	0.07	76.9-78.9
Pot residue		8.34	0.78	77.0-80.0

* Published values of boiling points (at 1 mm): methyl stearate 158.2 °C (Scott, Macmillan, and Melvin 1952); methyl arachidate 175 °C; methyl behenate 192 °C (corrected to 1 mm from Weitkamp's (1945) data at 1.95 mm).

† Micro-melting point after one crystallization from ethanol.

‡ Esters converted directly to hydroxamic acids. Weight of isolated acids calculated from yield of hydroxamic acid.

II. EXPERIMENTAL

All melting points, unless stated to be micro, were determined in a Herschberg apparatus using total immersion thermometers. The micro-melting points were determined on a hot stage using direct microscopic observation. The iodine values and saponification values were determined by the Official and Tentative Methods of the American Oil Chemists' Society (2nd

Ed., 1946). The hydroxyl values were determined by the semimicro-procedure of Ogg, Porter, and Willits (1945).

(a) *Isolation of the Saturated Acids.*—Forty bushels (about 720 kg) of Granny Smith apples, after storage at 20 °C for 6 weeks, were extracted whole with hot light petroleum, yielding 512 g of mixed wax and oil. The wax and oil were separated by crystallization from acetone as described previously (Huelin and Gallop 1951a, 1951b) yielding 210 g of oil. The oil smelt strongly of apples and had the following characteristics:

Acid value	24.5
Saponification value	136.7
Hydroxyl value	97.1
Iodine value	77.1
$n_D^{17.1}$	1.4853; $[\alpha]_D^{20} +1.2 \pm 0.2$ (c, 10.3 in acetone);
$E_{1\text{cm}}^{1\%}$	116 at 233.5 m μ (max.).

The oil was saponified by dissolving in 1 l. of 2N ethanolic potassium hydroxide. To minimize oxidation 10 g of ascorbic acid was added and nitrogen bubbled through the mixture, which was kept at room temperature for 48 hr; after dilution with water the unsaponifiable matter (68 g) was extracted with diethyl ether. As the unsaponifiable matter still had an appreciable saponification No., it was treated again with 300 ml 2N ethanolic potassium hydroxide and 3 g of ascorbic acid, held at 50 °C for 48 hr, diluted with water and again extracted with diethyl ether. Evaporation of the ether yielded 41.0 g of unsaponifiable matter which had a negligible saponification value. The aqueous solutions were acidified at 0 °C and extracted with diethyl ether. On evaporation of the ether 138.0 g of acids remained. The total acids had an acid value of 186.8 and an iodine value of 111.8. They were then treated three times with 1 l. of light petroleum and the insoluble material (hydroxy acids) was spun down in a centrifuge. This residue was soluble in chloroform and weighed 15 g or about 7% of the total oil. The acids soluble in light petroleum were then crystallized from acetone (10% solution) at -18 °C. The saturated acids (21.5 g, 10.3% of the oil) had an acid value of 180.0. They were esterified with diazomethane yielding methyl esters with an hydroxyl value of 19.2. The hydroxy esters were removed by dissolving the material in light petroleum, filtering off the insoluble material (0.8 g), and passing through a column of silica gel. 12.2 g of material was eluted with light petroleum and 0.2 g with chloroform. An accidental loss of some of the material occurred before it was chromatographed. The material eluted with light petroleum was considered to be methyl esters of the saturated acids free of hydroxy esters. This material was distilled in a spinning band fractionating column (Murray 1951). The band was 8 ft in length and the distillation conducted at 1 mm. Mineral oil (35.5 g) of boiling range 165-200 °C/1 mm was distilled with the esters and the fractions obtained are listed in Table 1.

(b) *Fraction 1.*—The methyl esters were converted directly to the hydroxamic acids which were partitioned on a cellulose column (Davenport 1955). They separated into two bands of elution volumes 440 and 750 ml respectively. Crystals from the first band melted at 104.6-106.9 °C (micro) undepressed by admixture with an authentic sample of stearohydroxamic acid. The second band yielded crystals, m.p. 101.4-103.0 °C (micro), undepressed by admixture with an authentic sample of palmitohydroxamic acid.

(c) *Fraction 5.*—Saponification yielded 0.51 g of acids which after recrystallization from light petroleum, benzene, and ethanol melted at 66.0-67.6 °C. The mixed m.p. with an authentic sample of stearic acid (m.p. 69.6-69.8 °C) was 68.0-68.8 °C. When crystallized by the technique of Weitkamp (1945), they formed rhombic plates with an acute angle of 55°, typical of *n*-fatty acid.

(d) *Fraction 11.*—The isolated acids after saponification were recrystallized once from ethanol, m.p. 64.0-64.6 °C. This material was then esterified with diazomethane and converted to the hydroxamic acids with alkaline hydroxylamine solution. Partition chromatography on a cellulose column separated the material into two bands of elution volumes 250 and 440 ml respectively. The first band yielded crystals, m.p. 106.5-108.5 °C (micro), which on admixture with an authentic sample of arachidohydroxamic acid (m.p. 109.8-110.5 °C) melted at

107.3–108.3 °C (micro). Crystals from the second band melted at 104.5–106.0 °C (micro), and on admixture with an authentic sample of stearohydroxamic acid (m.p. 105.5–107.0 °C) melted at 105.0–106.3 °C (micro).

(e) *Fraction 16*.—Saponification yielded 0.52 g of acids, which after one recrystallization from ethanol melted at 71.7–73.9 °C (micro). Recrystallization from ethanol and from hexane gave crystals, m.p. 72.8–73.4 °C. On admixture with an authentic sample of arachidic acid (m.p. 75.3–76.3 °C) they melted at 74.1–74.9 °C. This material also had the typical crystal form of an *n*-fatty acid.

(f) *Fraction 24*.—Saponification yielded 0.095 g of acids which after one recrystallization from ethanol melted at 78.6–79.0 °C. Mixed m.p. with an authentic sample of behenic acid (m.p. 77.9–78.3 °C) was 78.0–78.8 °C. This material also had the typical crystal form of an *n*-fatty acid. Fraction 27 also yielded material, m.p. 78.2–79.0 °C, which was undepressed by admixture with behenic acid.

(g) *Pot Residue*.—Saponification of the pot residue yielded 0.78 g of acids, which after recrystallization from acetone and from ethanol melted at 78.9–80.6 °C (acid value 150.9). Theoretical acid value for *n*-tetracosanoic acid (m.p. 84.15 °C) is 152.2.

III. ACKNOWLEDGMENTS

The author is indebted to Dr. F. E. Huelin for much helpful discussion and advice, to Mr. R. A. Gallop for the construction of the fractionating column and preliminary work on the problem, to Dr. F. B. Shorland for the gift of an authentic sample of arachidic acid, to Mr. R. Schoenfeld for the gift of an authentic sample of behenic acid, and to Mr. J. McGeorge for technical assistance.

IV. REFERENCES

- DAVENPORT, J. B. (1955).—*Chem. & Ind.* **1955**: 705.
HACKNEY, F. M. V. (1943).—*Proc. Linn. Soc. N.S.W.* **68**: 33.
HUELIN, F. E., and GALLOP, R. A. (1951a).—*Aust. J. Sci. Res. B* **4**: 526.
HUELIN, F. E., and GALLOP, R. A. (1951b).—*Aust. J. Sci. Res. B* **4**: 533.
MURRAY, K. E. (1951).—*J. Amer. Oil Chem. Soc.* **28**: 213.
OGG, C. L., PORTER, W. L., and WILLITS, C. O. (1945).—*Industr. Engng. Chem. (Anal.)* **17**: 394.
SCOTT, T. A., MACMILLAN, D., and MELVIN, E. H. (1952).—*Industr. Engng. Chem.* **44**: 172.
WEITKAMP, A. W. (1945).—*J. Amer. Chem. Soc.* **67**: 447.

THE PREPARATION AND CHARACTERIZATION OF SOME ALIPHATIC 2,4-DIENALS

By D. A. FORSS* and N. C. HANCOX†

[Manuscript received March 16, 1956]

Summary

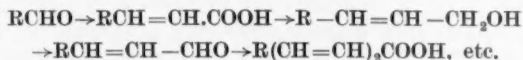
Three 2,4-dienals, 2,4-heptadienal, 2,4-nonadienal, and 2,4-hendecadienal, have been prepared synthetically for the first time, their semicarbazones, 2,4-dinitrophenylhydrazones and tetrahydroimidazole derivatives described, and ultraviolet absorption characteristics of the aldehydes and the two first-named derivatives recorded. The infra-red spectrum of 2,4-heptadienal is recorded and evidence presented for an all-*trans*-configuration.

I. INTRODUCTION

In connection with earlier work (Forss, Pont, and Stark 1955) on the substances responsible for the development of oxidation taints in milk, it was desirable to have some synthetic 2,4-dienals for comparison with substances isolated.

Of the homologous series of normal aliphatic dienals only the first two members, 2,4-pentadienal (Woods and Sanders 1946) and 2,4-hexadienal (cf. Kuhn and Hoffer 1930), have been synthesized, and these by methods not applicable to the general case. The object of the present work was to prepare representative members of the series in a state of reasonable purity by a method which could be applied at will to other members.

From the numerous synthetic sequences available for such synthesis, a procedure was chosen involving chain lengthening of a 2-enal by two carbon atoms in a Doebner synthesis with malonic acid, reduction of the resultant dienoic acid with lithium aluminium hydride to the dienol, and oxidation of the latter with manganese dioxide in an inert solvent. The procedure is theoretically capable of being carried through in a double sequence from the saturated aldehyde of carbon number four less than the desired product:



Such a synthesis was attempted from heptanal to undecadienal, but the overall yield was prohibitively low, and it was preferable to prepare the mono-unsaturated aldehyde by another method, of which the most general is by α -bromination and dehydrobromination from the saturated aldehyde.

* Dairy Research Section, C.S.I.R.O., Melbourne.

† Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Since quite small quantities of the final product were sufficient for our purpose, high overall yields were not a major consideration; moreover, time did not permit a detailed examination of the best conditions for each step. The biggest losses occurred in the Doebner synthesis and the manganese dioxide oxidation. Crombie (1955) reports a low yield (37%) of 2,4-decadienoic acid in the Doebner synthesis from octenal; the manganese dioxide oxidation is reported to give very good yields with higher polyene alcohols, but may be less effective when the conjugated chain is shorter. This step was nevertheless retained, in preference to other methods of oxidation, or conversion of the acid to the aldehyde by reduction of the carbazole derivative with lithium aluminium hydride (Wittig and Hornberger 1952), since the specificity of the manganese dioxide oxidation for allylic alcohols is a valuable feature for eliminating the possibility of contamination of the product with non-conjugated aldehydes which may result from the formation of some $\beta\gamma$ -unsaturated acid in the Doebner synthesis. For isolation of the final aldehyde from the crude reaction mixture (about 50% purity), use was made of the reaction with 1,2-dianilinoethane (Wanzlick and Löchel 1953) to give substituted tetrahydroimidazoles; these compounds are well suited for characterization and for regeneration of the pure aldehyde under mild conditions. The regenerated aldehydes were finally distilled *in vacuo* and their spectral characteristics determined without delay.

In theory, a 2,4-dienal should be capable of occurring in four stereoisomeric forms; however, no instance appears to have been reported of *cis-trans*-isomerism in *unsubstituted* 2-enals or their vinylogs (isomerism in such aldehydes substituted at the double bond is well known e.g. the citrals). Raphael and Sondheimer (1951) prepared *cis*-crotonaldehyde diethyl acetal but on hydrolysis obtained a product indistinguishable from ordinary *trans*-crotonaldehyde; they suggest that in the presence of acid the initially-formed labile *cis*-aldehyde passes readily to the *trans*-form through the mesomeric conjugate acid:



An extended mesomeric ion would likewise result in ready interconversion of the isomers of a dienal.

2,4-Pentadienal, though prepared from a cyclic compound, likewise appears to be *trans-trans* (Crombie, Harper, and Thompson 1951).

The Doebner synthesis is generally considered to give a *trans*-acid, and in view of this and the above considerations, it is probable that the aldehydes obtained in the present work are *trans-trans*. This conclusion is supported by an infra-red spectroscopic study of 2,4-heptadienal reported below.

The ultraviolet spectra of the aldehydes showed an intense broad maximum at 273.5 m μ (95% ethanol), with molar extinction coefficients ranging from 23,000 to 29,000; these values may be compared with the values of Blout and Fields (1948) for 2,4-hexadienal λ_{max} (alc.) 271 m μ , ϵ_{max} 24,600.

II. EXPERIMENTAL

Melting points are corrected. Microanalyses were carried out by the C.S.I.R.O. Micro-analytical Laboratory under the direction of Dr. K. W. Zimmermann.

2-Pentenal was prepared as described by Kuhn and Grundmann (1937), via *n*-valeraldehyde, 2-bromovaleraldehyde methyl acetal, and 2-pentenal dimethyl acetal. It had b.p. 122–124 °C/760 mm.

2-Heptenal was prepared from commercial heptaldehyde (from castor oil) purified through the bisulphite compound and redistilled (b.p. 151–152.5 °C/760 mm). Two different procedures were used: the method of Kuhn and Grundmann (loc. cit.), and that of Bedoukian (1949) involving bromination of the enol acetate. The latter gives a lower yield but is somewhat more convenient. The product in each case had b.p. 54–56 °C/15 mm.

2-Nonenal was prepared according to the directions of Scanlan and Swern (1940) by the Criegee oxidation of 9,10,12-trihydroxystearic acid obtained from castor oil. It had b.p. 70–72 °C/3 mm.

2,4-Heptadienoic Acid.—Malonic acid (18 g) and *n*-heptenal (12.5 g) were dissolved in 20 ml dry pyridine and the mixture allowed to stand at room temperature for 3 days with frequent shaking, and finally heated on a steam-bath until evolution of carbon dioxide had ceased (8–9 hr). After cooling, the mixture was poured into ice-cold 25% sulphuric acid, the crude heptadienoic acid extracted with ether, and purified by passage through 10% aq. NaOH, extraction to remove non-acidic material, and recovery into ether after reacidification. The acid obtained had b.p. 119–120 °C/10 mm, λ_{max} 255 m μ , ϵ 23,300. Yield 7 g, 37%. Crombie (1955) reports λ_{max} 257 m μ , ϵ 28,500 for *trans-trans*-2,4-decadienoic acid.

2,4-Heptadienol.—Heptadienoic acid (7 g) in 30 ml anhydrous ether was added dropwise (1 hr) to a slurry of lithium aluminium hydride (2 g) in 75 ml ether, so as to maintain gentle reflux, which was continued for a further hour after addition of the acid. The excess lithium aluminium hydride was then destroyed by addition of 2 ml of water, and the reaction mixture filtered from lithium aluminate under nitrogen pressure through sintered glass. The crude alcohol had λ_{max} 230 m μ , ϵ_{max} 24,500 indicating that the conjugated double bonds were substantially unaffected by the reduction. The material was used without further purification for the next step.

2,4-Heptadienal.—Crude heptadienol (5 g) dissolved in 200 ml of light petroleum was stirred with 40 g manganese dioxide prepared according to Attenburrow *et al.* (1952). After 4 hr at room temperature, the mixture was filtered and the solvent removed under nitrogen; the product had $E_{1\text{ cm}}^{1\%}$: 1050 at λ_{max} 273.5 m μ , indicating a dienal content of approximately 50%. Extending the reaction time to 18 hr did not improve this.

The above crude product (2 g) was added to a solution of 1,2-dianilinoethane (4 g) in 80 ml of methanol containing 0.8 ml of 50% acetic acid. Crystallization was induced by adding a few drops of water and cooling to 0 °C. Yield of 1,3-diphenyl-2-(2,4-hexadienyl)tetrahydroimidazole 1.8 g of colourless plates, which after two recrystallizations from methanol had m.p. 120.5–121.5 °C (Found: C, 82.8; H, 8.0; N, 9.5%. Calc. for $\text{C}_{21}\text{H}_{24}\text{N}_2$: C, 82.9; H, 7.9; N, 9.3%).

The aldehyde was regenerated from 1 g of the above tetrahydroimidazole by shaking with 50 ml of 10% HCl for 30 min, followed by extraction with chloroform. It was finally distilled *in vacuo*; b.p. 58–60 °C/5 mm, yield 200 mg (Found: C, 76.0; H, 9.5; O, 14.9%; λ_{max} (EtOH) 273.5 m μ ; ϵ_{max} 23,000. Calc. for $\text{C}_7\text{H}_{10}\text{O}$: C, 76.4; H, 9.1; O, 14.5%). It could be kept reasonably well under nitrogen at 0 °C, but appeared to polymerize over a period of weeks.

The semicarbazone and 2,4-dinitrophenylhydrazone were prepared by the usual methods and recrystallized from ethanol.

Semicarbazone, colourless pearly flakes, m.p. 188–190 °C, λ_{max} (EtOH) 293 m μ , ϵ_{max} 45,800 (Found: C, 57.6; H, 8.0; O, 9.2%. Calc. for $\text{C}_8\text{H}_{13}\text{ON}_3$: C, 57.5; H, 7.8; O, 9.6%).

2,4-Dinitrophenylhydrazones, orange-red needles, m.p. 155–156 °C, λ_{\max} . (EtOH) 389 m μ , ϵ_{\max} . 36,500 (Found: C, 54.2; H, 5.2; N, 19.6; O, 22.0%. Calc. for $C_{15}H_{14}O_4N_4$: C, 53.8; H, 4.8; N, 19.3; O, 22.1%).

The remaining two aldehydes were prepared by analogous procedures, the syntheses being carried through without special characterization of intermediates.

2,4-Nonadienal.—2-Heptenal (17 g) and malonic acid (15 g) in 15 ml pyridine, yielded 11.5 g (48%) crude nonadienoic acid. The crude acid in 50 ml of ether reduced with 4 g of lithium aluminium hydride in 150 ml of ether gave 9 g (91%) of nonadienol. This alcohol, stirred with 60 g manganese dioxide in 250 ml of light petroleum for 4 hr gave 9 g of crude aldehyde with $E_{1\text{ cm}}^{1\%}$ 925 at λ_{\max} . 273.5 (40% dienal). From 3 g of the crude aldehyde 1.7 g of *1,3-diphenyl-2-(2,4-octadienyl)tetrahydroimidazole* was prepared, which after recrystallization from methanol had m.p. 113–114 °C (Found: C, 83.4; H, 8.7; N, 8.6%. Calc. for $C_{23}H_{22}N_2$: C, 83.1; H, 8.4; N, 8.4%).

The pure aldehyde was obtained from 1.28 g of derivative by shaking with 60 ml of 10% HCl and extraction with light petroleum (40–60 °C) followed by distillation *in vacuo*. Yield 220 mg, b.p. 72–74 °C/3 mm, λ_{\max} . (EtOH) 273.5 m μ , ϵ_{\max} . 26,000 (Found: C, 77.9; H, 10.5%. Calc. for $C_9H_{14}O$: C, 78.3; H, 10.1%).

Semicarbazone from ethanol, m.p. 182–183 °C, λ_{\max} . 294 m μ , ϵ_{\max} . 41,700 (Found: C, 61.7; H, 9.4; N, 21.5%. Calc. for $C_{10}H_{17}N_3O$: C, 61.6; H, 8.7; N, 21.0%).

2,4-Dinitrophenylhydrazones from ethanol, m.p. 136–138 °C, λ_{\max} . 390 m μ , ϵ_{\max} . 39,000 (Found: C, 56.7; H, 6.0; N, 17.6%. Calc. for $C_{15}H_{15}O_4N_4$: C, 56.6; H, 5.7; N, 17.6%).

2,4-Hendecadienal.—2-Nonenal (10 g) and malonic acid (7.5 g) in 10 ml of pyridine gave 8.2 g (66%) of hendecadienoic acid, which, on reduction with lithium aluminium hydride (4 g) in 150 ml ether gave 6 g of crude dienal. On shaking for 2 hr with manganese dioxide (40 g) in 150 ml of light petroleum 4 ml of crude aldehyde was obtained with $E_{1\text{ cm}}^{1\%}$ 850 (49% dienal). From 1.5 g of this was obtained 1.05 g of *1,3-diphenyl-2-(2,4-decadienyl)tetrahydroimidazole*, which after recrystallization from methanol had m.p. 101–102 °C (Found: C, 83.2; H, 9.1; N, 7.8%. Calc. for $C_{25}H_{24}N_2$: C, 83.3; H, 8.9; N, 7.8%). The pure aldehyde, regenerated as before, had b.p. 80–81 °C/1 mm, λ_{\max} . 273.5, ϵ_{\max} . 29,000 (Found: C, 79.1; H, 11.0; O, 10.0%. Calc. for $C_{11}H_{18}O$: C, 79.5; H, 10.8; O, 9.6%).

Semicarbazone from ethanol, m.p. 183–184 °C, λ_{\max} . 294 m μ , ϵ_{\max} . 47,700 (Found: C, 64.6; H, 9.5; N, 18.8%. Calc. for $C_{12}H_{21}N_3O$: C, 64.6; H, 9.4; N, 18.8%).

2,4-Dinitrophenylhydrazones from ethanol, m.p. 131–132 °C, λ_{\max} . 389 m μ , ϵ_{\max} . 37,000 (Found: C, 59.4; H, 6.6; N, 15.3%. Calc. for $C_{17}H_{22}O_4N_4$: C, 59.0; H, 6.4; N, 15.3%).

Note on the Infra-Red Spectrum of 2,4-Heptadienal*

The spectrum of the liquid has been measured over the 2–15 μ region, and that of a solution in chloroform over the 6 μ region.

The absorption (in cm^{-1}) in the 6 μ region is very similar to that reported for 2,4-hexadienal by Blout, Fields, and Karplus (1948):

2,4-Hexadienal (vap.)	1608(w)	1650(m)	1705(v.s.)
„ (CHCl ₃ soln.)	1608(w)	1642(s)	1677(v.s.)
2,4-Heptadienal (vap.)	1602(w)	1644(s)	1692(v.s.)
„ (CHCl ₃ soln.)	1602(w)	1642(s)	1684(v.s.)

No indication was found of the presence of acid or ketonic impurities.

The stereochemical configuration of the two double bonds has been deduced from a comparison of the 7 and 10 μ regions of the spectrum with those of conjugated diene acids (Jackson *et*

* By J. B. Willis.

al. 1952; Celmer and Solomons 1953) and those of diphenylpolyenes (Lunde and Zechmeister 1954). Since few previous infra-red studies have been made on diene aldehydes, it has to be assumed that the presence of a conjugated C=O group will not affect the C—H deformation frequencies of the diene system any more than the presence of another conjugated C=C group would do.

In the 7 μ region *cis-cis*- or *cis-trans*-polyenes absorb at 1410–1430 cm^{-1} , such absorption being absent in *trans-trans*-compounds (Lunde and Zechmeister 1954). The present compound has no marked absorption in this region, and, therefore, probably has the *trans-trans*-configuration.

In the 10 μ region *trans-trans*-compounds absorb at about 990 cm^{-1} while *cis-trans*-compounds have, in addition, a band at 945–960 cm^{-1} , and *cis-cis*-compounds have no bands at all in this neighbourhood. The present compound has a peak at 990 cm^{-1} , but no absorption between 980 and 930 cm^{-1} . This again indicates a *trans-trans*-configuration. Absence of isolated double bonds with a *trans*-configuration is indicated by absence of absorption near 965 cm^{-1} .

In the 12–14.5 μ region, Lunde and Zechmeister (1954) found bands characteristic of *cis*-double bonds. The present compound has no absorption in this region, and this is confirmatory evidence for an all-*trans*-configuration.

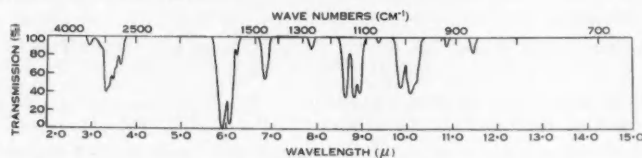


Fig. 1.—Infra-red absorption spectra of 2,4-heptadienal.

The complete spectrum of the liquid is shown in Figure 1.

III. ACKNOWLEDGMENTS

The authors' thanks are due to Dr. H. H. Hatt for helpful discussion, and to Mr. E. A. Dunstone for technical assistance.

IV. REFERENCES

- ATTENBURROW, J., CAMERON, A. F. B., CHAPMAN, J. H., EVANS, R. M., HEMS, B. A., JANSEN, A. B. A., and WALKER, T. (1952).—*J. Chem. Soc.* **1952** : 1104.
 BEDOUKIAN, P. Z. (1949).—"Organic Syntheses." Coll. Vol. **3** : 127.
 BLOUT, E. R., and FIELDS, M. (1948).—*J. Amer. Chem. Soc.* **70** : 191.
 BLOUT, E. R., FIELDS, M., and KARPLUS, R. (1948).—*J. Amer. Chem. Soc.* **70** : 194.
 CELMER, W. D., and SOLOMONS, I. A. (1953).—*J. Amer. Chem. Soc.* **75** : 3430.
 CROMBIE, L. (1955).—*J. Chem. Soc.* **1955** : 1007.
 CROMBIE, L., HARPER, S. H., and THOMPSON, D. (1951).—*J. Chem. Soc.* **1951** : 2906.
 FORSS, D. A., PONT, E. G., and STARK, W. (1955).—*J. Dairy Res.* **22** : 91, 102.
 JACKSON, J. E., PASCHKE, R. F., TOLBERG, W., BOYD, H. M., and WHEELER, D. H. (1952).—*J. Amer. Oil Chem. Soc.* **29** : 229.
 KUHN, R., and GRUNDMANN, C. (1937).—*Ber. dtsch. chem. Ges.* **70** : 1894.
 KUHN, R., and HOFFER, M. (1930).—*Ber. dtsch. chem. Ges.* **63** : 2164.
 LUNDE, K., and ZECHMEISTER, L. (1954).—*Acta Chem. Scand.* **8** : 1421.
 RAPHAEL, R. A., and SONDEHEIMER, F. (1951).—*J. Chem. Soc.* **1951** : 2694.
 SCANLAN, J. T., and SWERN, D. (1940).—*J. Amer. Chem. Soc.* **62** : 2309.
 WANZLICK, H. W., and LÖCHEL, W. (1953).—*Chem. Ber.* **86** : 1463.
 WITTIG, G., and HORNBERGER, P. (1952).—*Liebigs Ann.* **577** : 11.
 WOODS, G. F., and SANDERS, H. (1946).—*J. Amer. Chem. Soc.* **68** : 2483.

SHORT COMMUNICATIONS

A.C. WAVES AND D.C. POLAROGRAPHIC MAXIMA*

By B. BREYER† and H. H. BAUER†

It is well known that under some conditions, the D.C. polarographic step of nitrobenzene shows a maximum. Here, it is shown that the nature of the corresponding A.C. wave depends on whether or not such a maximum is present.

For instance, in "Universal" buffer (Prideaux and Ward 1924) of pH 1.8, the D.C. polarogram shows two steps, the first, corresponding to a four-electron reduction of nitrobenzene to phenylhydroxylamine, and the second, to a two-electron reduction of the latter to aniline (cf., for example, Seagers and Elving

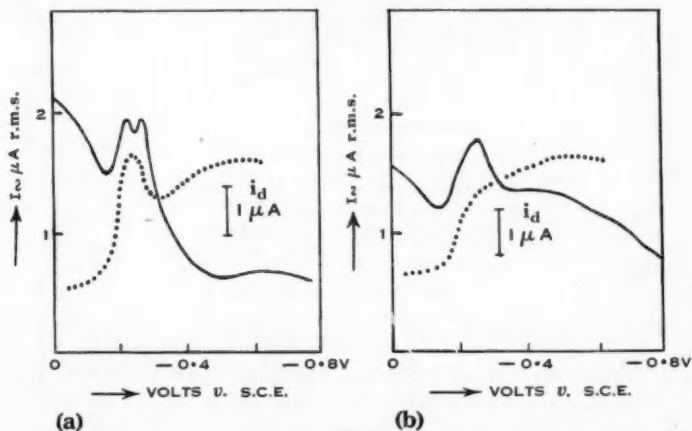


Fig. 1.—A.C. (—) and D.C. (...) polarograms of nitrobenzene, $2 \times 10^{-3}M$.

(a) In "Universal" buffer pH 1.8.

(b) In "Universal" buffer pH 1.8 + 0.5M potassium nitrate.

1951); the first step has a maximum. The A.C. curve shows two peaks corresponding in potential to the first D.C. step (Fig. 1 (a)). When the solution contains 0.5M potassium nitrate in addition to the buffer, the D.C. maximum is suppressed and the corresponding A.C. curve (Fig. 1 (b)) appears to have only a single peak in the region of the first D.C. step. On close examination, however, also this wave is shown to be a composite one (see below).

* Manuscript received April 16, 1956.

† Section of Agricultural Chemistry, Faculty of Agriculture, University of Sydney.

At pH 7.3, with low concentrations of nitrobenzene in "Universal" buffer, no maximum is present on the D.C. polarogram and the A.C. wave is well defined. At higher concentrations a maximum appears on the D.C. step, but the A.C. wave is not distorted; however, it increases in height far more than would be expected. Thus for an increase in concentration of nitrobenzene from 10^{-4} M to 3×10^{-4} M, the magnitude of the D.C. diffusion current increases to three times its former value, while the A.C. wave increases in height by about five times (Fig. 2).

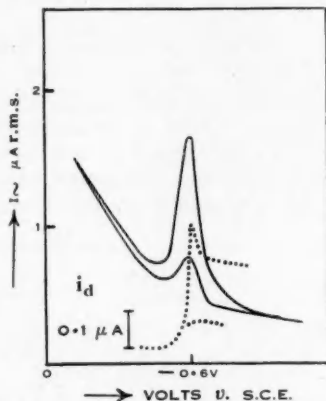


Fig. 2.—A.C. (—) and D.C. (···) polarograms of nitrobenzene in "Universal" buffer pH 7.3. Lower curves 10^{-4} M, upper curve 3×10^{-4} M.

Summarizing

The process responsible for the appearance of a maximum on the D.C. polarographic step of nitrobenzene also gives rise to an increase in the alternating current. This increase might appear as a separate peak on the A.C. curve (as at pH 1.8, see Fig. 1) or the current increase might occur at the same potential as the main A.C. wave, thus adding to its height (as at pH 7.3, see Fig. 2).

Even when no D.C. maximum is present, the A.C. waves of nitrobenzene appear, on close examination, to be composite; they show a kink which, though small, is invariably present (Fig. 3). This is best seen when smaller alternating voltages than the usual 15 mV r.m.s. are used, and when readings are taken at small intervals of applied direct potential (5 mV or less).

This kink may be due to:

- (i) An incipient maximum; that is, even where no maximum is visible on the D.C. step, the process which gives rise to maxima may nevertheless be proceeding, albeit to a minor extent.
- (ii) A combined polarographic-tensammetric process; in other words, the A.C. wave may in fact consist of two waves, the one a result of the reduction process and the other brought about by a concomitant

adsorption process. Such combined processes have been discussed in detail elsewhere (Breyer, Bauer, and Hacobian 1954).

- (iii) A reduction process occurring in more than one step, since the overall transfer of four electrons is involved. Thus the potential of the kink and the peak potential of the main A.C. wave might correspond to different stages in the reduction of nitrobenzene to phenylhydroxylamine.

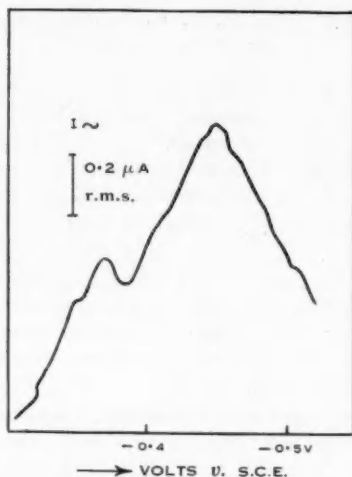


Fig. 3.—A.C. wave of 4×10^{-4} M nitrobenzene at pH 4.9. Superposed alternating voltage 5 mV r.m.s.

Possibilities (i) and (ii) obviously may be correlated with the observation reported here, namely, the production of an A.C. peak by the process which gives rise to D.C. maxima. The third possibility seems of great theoretical interest, since it would supply information about the mechanism of the particular reduction process.

Further experimental work is needed to decide which of the proposed hypotheses is valid.

References

- BREYER, B., BAUER, H. H., and HACOBIAN, S. (1954).—*Aust. J. Chem.* **8**: 312.
 PRIDEAUX, E. B. R., and WARD, A. T. (1924).—*J. Chem. Soc.* **125**: 426.
 SEAGERS, W. J., and ELVING, P. J. (1951).—*Proc. 1st Int. Congr. Polarography Prague* **1**: 281.

TRITERPENOID COMPOUNDS*†

III. PHILLYRIGENIN

By A. L. BECKWITH,‡ A. R. H. COLE,§ J. C. WATKINS,§
and D. E. WHITE§

The investigation of the sapogeninins of *Pittosporum phillyraeoides* DC. was undertaken in view of the occurrence of polyhydroxytriterpenoids in the related *P. undulatum* Ventenat (Cornforth and Earl 1938; Cole *et al.* 1955). Two crystalline compounds were isolated and one of these proved to be identical with pittosapogenin, $C_{30}H_{52}O_6$, as obtained from *P. undulatum* (Cole *et al.* 1955).

The second compound, m.p. 339–341 °C, analysed for $C_{30}H_{48}O_4$ and has been named phillyrigenin. It contains two hydroxyl groups, which have been characterized by the preparation of a number of acyl derivatives, and its absorption in the infra-red confirms their presence and also indicates the presence of a 6-membered lactone ring. This was confirmed by saponification with alkali at 200 °C, which yielded a mixture from which an unsaturated dihydroxy acid was isolated as its methyl ester.

Oxidation of phillyrigenin with chromic acid yielded a keto acid, indicating that one hydroxyl group was primary and one secondary. The infra-red absorption spectra of the monoacetates indicate that the secondary hydroxyl is free in monoacetate A (m.p. 242 °C) and the primary hydroxyl free in monoacetate B (m.p. 348 °C). Attempts to reduce the lactone grouping with lithium aluminium hydride were unsuccessful.

Experimental

Melting points were determined in evacuated capillaries and are corrected. Light petroleum refers to the fraction b.p. 40–90 °C. Microanalyses were carried out in the C.S.I.R.O. Micro-analytical Laboratory. Rotations and I.R. spectra are in chloroform solution unless otherwise indicated.

(a) *Extraction*.—Air-dried leaves and terminal stems (3 kg) of *P. phillyraeoides* collected from Rottnest I., Western Australia, were powdered and extracted with ether (3 × 6 l.) during 9 days. This yielded a neutral waxy product (30 g), alkali-soluble material (3 g), and insoluble sodium salts (8 g) which were not investigated further.

The residue from the ether extraction was treated with 50% aqueous ethanol (5 × 4 l.) during 15 days, and the combined extracts concentrated to 7.5 l. and hydrolysed by refluxing for 6 hr with conc. HCl (500 ml). A brown precipitate (355 g) separated on cooling and yielded 300 g of chloroform-soluble material.

* Manuscript received February 15, 1956.

† Part II of this series is on p. 406.

‡ Organic Chemistry Department, University of Adelaide; present address: Dyson Perrins Laboratory, Oxford.

§ Chemistry Department, University of Western Australia, Nedlands, W.A.

The chloroform extract (185 g) in hot methanol (1300 ml) was treated with charcoal, and on cooling, a crystalline compound (19 g), m.p. 329–333 °C, separated. Further quantities of less pure material (18 and 7 g) were obtained on concentration to 700 and 300 ml respectively. Crystallization from methanol (5 times) yielded large rectangular plates of *phillyrigenin*, m.p. 339–341 °C, $[\alpha]_D^{23} + 23^\circ$ (c, 0.833) containing solvent of crystallization which was lost either at room temperature or on heating (Found: C, 76.3, 76.2; H, 10.1, 9.8%. Calc. for $C_{20}H_{18}O_4$: C, 76.2; H, 10.2%). *Phillyrigenin* was soluble in pyridine, chloroform, and acetic acid, moderately soluble in methanol, and sparingly soluble in ether, benzene, carbon tetrachloride, and light petroleum. Addition of sulphuric acid to a solution in acetic anhydride gave a yellow colour changing to orange and red. It gave no colour with ferric chloride or with tetranitromethane in chloroform and did not react with hydroxylamine hydrochloride in pyridine nor with acetone in the presence of either HCl or H_2SO_4 . After treatment with lithium aluminium hydride in boiling ether for 8 hr *phillyrigenin* was recovered unchanged. *Phillyrigenin* absorbed at 3618 cm^{-1} (ϵ_{max} , 110; 2 OH groups) and 1735 cm^{-1} (δ -lactone).

The methanol solution remaining after the *phillyrigenin* crystallized was diluted to 1 l. with methanol, refluxed for 1 hr with aqueous KOH (50%; 250 ml), cooled, and poured into water. The precipitate which separated, yielded a mixture of plates and needles from methanol (2 crops; 32 g). Extraction of this material with boiling chloroform (1500 ml) during 1 hr yielded more *phillyrigenin* (5.5 g; m.p. 328–331 °C on crystallization from methanol), and the residue (23 g) then formed clusters of stout needles, m.p. 306–308 °C, from methanol (Found: C, 70.8, 70.8; H, 10.4, 10.0%. Calc. for $C_{20}H_{18}O_4$: C, 70.8; H, 10.3%). Comparison (mixed m.p. and I.R. absorption of a "Nujol" mull) with a sample of *pittosapogenin* isolated from *P. undulatum* (Cole *et al.* 1955) showed it to be identical with this material.

A similar extraction of dried powdered fruits using aqueous methanol instead of aqueous ethanol yielded slightly less *phillyrigenin* (1.1%) and more *pittosapogenin* (1.25%).

(b) *Phillyrigenin Diacetate*.—*Phillyrigenin* (100 mg), acetic anhydride (3 ml), and pyridine (0.3 ml) were refluxed for 1.5 hr, cooled, and poured into water. After washing, the precipitated *diacetate* formed colourless hexagonal plates (82 mg), m.p. 252 °C, $[\alpha]_D^{15} + 21^\circ$ (c, 0.8) from aqueous ethanol (Found: C, 73.3; H, 9.3; Ac, 14.8%; mol. wt. (Rast), 476. Calc. for $C_{24}H_{22}O_6$: C, 73.3; H, 9.4; Ac, 15.5%; mol. wt., 556.8). On saponification with 3.5% ethanolic KOH, *phillyrigenin* was regenerated.

(c) *Phillyrigenin Monoacetates*.—Acetic anhydride (175 mg) in dry pyridine (5 ml) was added dropwise with shaking to a solution of *phillyrigenin* (500 mg) in pyridine (10 ml) at room temperature. Next day the mixture was poured into dil. HCl and the resultant gum taken up in chloroform. After washing, the solvent was removed and the crude product (510 mg) chromatographed on alumina (15 g; activity III–IV). The following fractions were eluted:

- (i) With 1:1 hexane/benzene, *phillyrigenin diacetate* (63 mg), m.p. and mixed m.p. 252 °C.
- (ii) With 1:1 hexane/benzene, *phillyrigenin monoacetate A* (143 mg) which formed colourless needles, m.p. 242 °C, $[\alpha]_D^{15} + 16^\circ$ (c, 0.77) from aqueous ethanol (Found: C, 74.6; H, 9.5%. Calc. for $C_{22}H_{20}O_5$: C, 74.7; H, 9.8%) and absorbed at 3614 cm^{-1} (ϵ_{max} , 60).
- (iii) With benzene, *phillyrigenin monoacetate B* (95 mg) which formed colourless needles, m.p. 348 °C, $[\alpha]_D^{15} + 31^\circ$ (c, 0.41) from ethanol (Found: C, 74.8; H, 10.0%) and absorbed at 3625 cm^{-1} (ϵ_{max} , 70).
- (iv) With 1:1 benzene/chloroform, unchanged *phillyrigenin* (210 mg), m.p. and mixed m.p. 333 °C.

(d) *Phillyrigenin Dibenzoate*.—Benzoyl chloride (3 ml) was added gradually with shaking to a solution of *phillyrigenin* (0.5 g) in pyridine (7 ml), refluxed for 1 hr, cooled, and poured into dil. H_2SO_4 . The red oil, which separated, was taken up in ether, washed with acid and with sodium carbonate. After removal of the ether the residue (0.55 g) crystallized from ethanol and

formed needles of *phillyrigenin dibenzoate*, m.p. 267–268 °C, $[\alpha]_D^{25} + 20^\circ$ (c, 1.02) from 1 : 4 chloroform/methanol (Found : C, 77.5; H, 8.3%. Calc. for $C_{44}H_{38}O_8$: C, 77.6; H, 8.3%). The same product was obtained in 24 hr at room temperature instead of refluxing for 1 hr.

(e) *Phillyrigenin Diformate*.—Phillyrigenin (0.5 g) in 90% formic acid (10 ml) was refluxed for 2 hr. On cooling and pouring into water, the product formed plates of *phillyrigenin diformate*, m.p. 306–307 °C, from methanol (Found : C, 73.2; H, 9.2%. Calc. for $C_{32}H_{24}O_8$: C, 72.7; H, 9.2%).

(f) *Cathylation of Phillyrigenin*.—Ethyl chloroformate (0.6 ml) was added dropwise with cooling and shaking to a solution of phillyrigenin (200 mg) in pyridine (8 ml). Next day the red solution was diluted with water and the gummy precipitate repeatedly washed with warm dil. HCl, and then with water. Chromatography on alumina (10 g; activity III–IV) yielded on elution with 1 : 1 hexane/benzene *phillyrigenin dicathylate* (155 mg) which formed needles, m.p. 214 °C, $[\alpha]_D^{20} + 72^\circ$ (c, 0.41) from aqueous ethanol (Found : C, 70.4; H, 9.1%. Calc. for $C_{36}H_{28}O_8$: C, 70.1; H, 9.2%) and with benzene a *phillyrigenin monocathylate* (70 mg) which formed needles (containing solvent of crystallization), m.p. 288 °C, $[\alpha]_D^{20} + 40^\circ$ (c, 0.2) from aqueous ethanol (Found : C, 72.3; H, 9.6%. Calc. for $C_{33}H_{22}O_8$: C, 72.8; H, 9.6%). Attempted cathylation in dioxan-pyridine yielded only unchanged phillyrigenin.

(g) *Phillyrigenin Dimesylate*.—A solution of phillyrigenin (200 mg) and methane sulphonyl chloride (0.4 ml) in pyridine (3 ml) after 48 hr at room temperature was diluted with dil. HCl and the red precipitate washed with water and dried. It formed laths of *phillyrigenin dimesylate* (145 mg), m.p. c. 160 °C (variable with decomp.), $[\alpha]_D^{15} + 17^\circ$ (c, 0.42) from ethanol (Found : C, 61.3; H, 8.1%. Calc. for $C_{32}H_{22}O_8S_2$: C, 61.1; H, 8.1%).

(h) *Phillyrigenin Ditosylate*.—Phillyrigenin (500 mg), *p*-toluenesulphonyl chloride (500 mg), and pyridine (5 ml) treated as in (g) above, yielded *phillyrigenin ditosylate* (680 mg) as rhombs, m.p. c. 160 °C (variable with decomp.), $[\alpha]_D^{15} + 14^\circ$ (c, 0.72) from methanol (Found : C, 67.8; H, 8.1%. Calc. for $C_{48}H_{42}O_8S_2$: C, 67.5; H, 8.0%).

(i) *Oxidation of Phillyrigenin*.—Phillyrigenin (510 mg) in acetic acid (10 ml) was added dropwise with stirring to a solution of chromium trioxide (400 mg) in acetic acid (30 ml) at room temperature. After 24 hr, the mixture was poured into water and the crude *keto acid* (310 mg) collected. It formed colourless needles, m.p. c. 400 °C, $[\alpha]_D^{25} + 68^\circ$ (c, 0.6) from chloroform/methanol (Found : C, 74.3; H, 9.1%. Calc. for $C_{30}H_{24}O_5$: C, 74.4; H, 9.2%).

Treatment of the acid (75 mg) in ethanol (5 ml) and KOH soln. (20%; 5 ml) at 40 °C with methyl sulphate (10 g) formed the *methyl ester* which was collected next day. It formed colourless needles (55 mg), m.p. 252 °C, $[\alpha]_D^{25} + 68^\circ$ (c, 0.56) from aqueous ethanol or methylene chloride-methanol (Found : C, 74.7; H, 9.3%. Calc. for $C_{31}H_{26}O_5$: C, 74.7; H, 9.3%).

(j) *Saponification of Phillyrigenin*.—A solution of phillyrigenin (1 g) and KOH (36 g) in diethylene glycol (120 ml) was refluxed for 5 hr, cooled, poured into water, acidified, and extracted with ether. On treatment of the ether solution with 10% NaOH soln. a sodium salt separated. This was filtered, dissolved in hot methanol (100 ml), and HCl (10%; 3 ml) and water added, until crystallization began. The product (250 mg) formed thin leaflets, m.p. 277–278 °C, from chloroform (Found : C, 75.3; H, 10.1%. Calc. for $C_{30}H_{26}O_5$: C, 73.4; H, 10.3%. Calc. for $C_{30}H_{24}O_4$: C, 76.2; H, 10.2%), which gave a yellow colour with tetranitromethane and hence appears to be a mixture of trihydroxy- and unsaturated dihydroxy-acids.

Treatment of the mixture (230 mg) in ether-methanol (1 : 1; 8 ml) with diazomethane (from 300 mg *N*-nitrosomethylurea) in ether (15 ml) and chromatography of the product on alumina (6 g; activity III) yielded *methyl dihydroxyphillyrigenate* (113 mg) on elution with benzene (145 ml). It formed colourless prisms, m.p. 224–226 °C, from benzene-light petroleum (Found : C, 76.9; H, 9.9%. Calc. for $C_{31}H_{26}O_4$: C, 76.5; H, 10.4%) and gave a yellow colour with tetranitromethane in chloroform. It absorbed in CCl_4 at 3634 cm^{-1} (ϵ_{max} , 90; 2 OH groups), 3023 and 1671 cm^{-1} (trisubstituted double bond), and 1733 cm^{-1} (methyl ester).

The authors are indebted to the University of Western Australia for grants from its Research Fund, to the Nuffield Foundation for the infra-red spectrometer and for a Fellowship (to A.R.H.C.), and to Professor A. Killen Macbeth for laboratory facilities (for A.L.B.).

References

- COLE, A. R. H., DOWNING, D. T., WATKINS, J. C., and WHITE, D. E. (1955).—*Chem. & Ind.* 1955 : 254.
CORNFORTH, J. W., and EARL, J. C. (1938).—*J. Proc. Roy. Soc. N.S.W.* 72 : 249.

THE OCCURRENCE OF LEDOL IN *PHEBALIUM SQUAMEUS* LABILL.*

By F. N. LAHEY† and J. A. LAMBERTON‡

The bark of the tree *Phebalium squameus* Labill., family Rutaceae, known popularly as "Satinwood", contains a crystalline, easily isolated sesquiterpene alcohol, which has been identified as ledol. Ledol was first isolated (Tropp 1875; Hjelt and Collan 1882) from the leaves and flowering tops of *Ledum palustre* L., a member of the family Ericaceae. Through the kindness of Professor N. J. Toivonen and Professor G. A. Nyman of the University of Helsinki, we have been able to compare our material with ledol obtained from that source by Professor Nyman. Hasenfratz (1928) has also reported the occurrence of ledol in *Sphacele parviflora* L., family Labiatae, but in this instance the identification depends on similarity of properties only.

The physical properties of the ledol from *P. squameus* are in close agreement with those given in the literature, and its identification is based on the mixed melting point determination and comparison of the infra-red absorption spectra. Ledol is a tertiary alcohol, and so readily dehydrated that derivatives cannot be prepared by the usual methods. We have been unable to obtain the crystalline chromate reported by Wienhaus (1914), and the hydrocarbon obtained by formic acid dehydration differs in its optical rotation from that reported by Kir'yalov (1949).

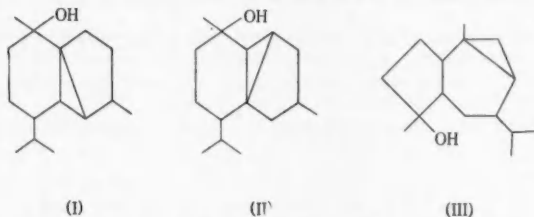
Komppa and Nyman (1938) proposed alternative formulae I and II for ledol, based on the observation that dehydrogenation gave both cadalene and an azulene. Kir'yalov (1953) has made an extensive study of the degradation products of ledol and claimed that formulae I and II were erroneous and that ledol was really 1,4-dimethyl-7-isopropylbicyclo[5,3,0]-1-decalol with a cyclopropane ring between the 4 and 6 positions (III).

* Manuscript received January 11, 1956.

† Chemistry Department, University of Queensland.

‡ Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Both I and III are in accord with the formation of 8-guaiazulene from ledol and its derivatives (Nyman and Mikander 1941; Kir'yalov 1953). Formula III, however, is unlikely because the infra-red absorption spectrum of ledol lacks the absorption band in the 3024–3058 cm^{-1} region, which Cole (1954) has found to be characteristic of a cyclopropane having an unsubstituted CH_2 group included in the ring. The presence of a tertiary hydroxyl group is



supported by the existence of a strong absorption band at 1115 cm^{-1} . Zeiss and Tsutsui (1953) found the characteristic C—O stretching frequency in 1-methylcyclohexan-1-ol, for instance, to lie at 1117 cm^{-1} , whereas the corresponding bands for primary and secondary alcohols lie at much lower frequencies.

The evidence for the structure of ledol is therefore inconclusive.

Experimental

Dry, milled bark of *P. squameus* (1.5 kg) was extracted by percolation with cold ether. The oily residue remaining after evaporating the ether was distilled under reduced pressure. After a small forerun of low boiling material, crude ledol (14–15 g) distilled and crystallized. It was purified by crystallization from light petroleum. Alternatively, ledol may be obtained by steam distillation of the material extracted by cold ether or methanol.

Purified ledol (10–11 g) melted at 104–105 °C (uncorr.) and this m.p. was undepressed by admixture with an authentic sample of ledol (m.p. 104–105 °C, uncorr.) from *L. palustre* (Found: C, 80.8; H, 11.8%. Calc. for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.0; H, 11.8%). The solution in ethanol has a slight positive rotation, $[\alpha]_D^{20} +4^\circ$ (c, 2.01 in ethanol). The literature gives: m.p., 105–106.5 °C (Kir'yalov 1949), $[\alpha]_D +7.98^\circ$ (Hjelt and Collan 1882), $[\alpha]_D +0.5^\circ$ (Kir'yalov 1949), (10% solution in ethanol).

Ledol has a pleasant smell and a marked tendency to sublime under reduced pressure and on warming, when it forms long needle-shaped crystals. A solution in ethanol showed no measurable ultraviolet absorption. Ledol is very resistant to oxidation. It was recovered unchanged after ozonolysis in acetic acid solution and after heating with potassium permanganate in acetone. It did not give a colour with a solution of tetranitromethane in chloroform.

(a) *Dehydration of Ledol*.—Attempts to prepare derivatives of the alcohol group caused dehydration. Dehydration was carried out in the ways described by Kir'yalov (1949) for the preparation of ledene and leddiene.

(i) Heating ledol with ethanolic sulphuric acid gave a hydrocarbon, b.p. 94–96 °C (1.5 mm), having $[\alpha]_D^{20} +46^\circ$ (c, 1.94 in ethanol) (Found: C, 87.9; H, 11.8%. Calc. for $\text{C}_{13}\text{H}_{24}$: C, 88.2; H, 11.8%). For ledene, Kir'yalov gives b.p. 110–113 °C (3 mm), $[\alpha]_D^{16} +48.43^\circ$ (10% solution in ethanol).

(ii) Heating ledol with formic acid gave an isomeric hydrocarbon having b.p. 92–95 °C (1.5 mm); n_D^{20} , 1.4973; $[\alpha]_D^{20} -11.2^\circ$ (c, 2.32 in ethanol) (Found: C, 87.8; H, 11.8%). It gave a blue to purple colour with bromine in acetic acid or chloroform. For leddiene, Kir'yalov gives b.p. 103–104 °C (3 mm); n_D^{20} , 1.4971, $[\alpha]_D^{17} +36.5^\circ$ (10% solution in ethanol).

The authors wish to thank Dr. J. B. Willis for the infra-red spectra measurements.

References

- COLE, A. R. H. (1954).—*J. Chem. Soc.* **1954**: 3807.
HASENFRATZ, V. (1928).—*C.R. Acad. Sci. Paris* **137**: 903.
HJELT, E., and COLLAN, U. (1882).—*Ber. dtsh. chem. Ges.* **15**: 2500.
KIR'YALOV, N. P. (1949).—*J. Gen. Chem. Moscow* **19**: 2123. (*Chem. Abstr.* **43**: 1155.)
KIR'YALOV, N. P. (1953).—*Sbornik Statei Obshchei Khim.* **2**: 1617. (*Chem. Abstr.* **49**: 5389.)
KOMPPA, G., and NYMAN, G. A. (1938).—*C.R. Lab. Carlsberg* **22**: 272.
NYMAN, G., and MIKANDER, G. A. (1941).—*Suomen. Kem. B* **14**: 3.
TROFF, I. (1875).—*Ber. dtsh. chem. Ges.* **8**: 542.
WIENHAUS, H. (1914).—*Ber. dtsh. chem. Ges.* **47**: 330.
ZEISS, H. H., and TSUTSUI, M. (1953).—*J. Amer. Chem. Soc.* **75**: 897.

CHEMICAL CONSTITUENTS OF THE LUMINESCENT FUNGUS *PLEUROTUS LAMPAS* BERK.*

By J. A. LAMBERTON†

There are numerous descriptive accounts of the luminescence of the large fungus *Pleurotus lampas* Berk. (synonyms *P. nidiformis* Berk., *P. candescens* F. Muell.; family Agaricaceae), but no chemical examination of this fungus appears to have been made. In March 1955, fruiting bodies of *P. lampas* were collected at Cumberland Valley, near Marysville, with the object of isolating any unusual substances which might take part in the luminescence reaction. Some of the large specimens, which did not luminesce in the dark, were examined by Professor E. I. McLennan and identified as immature *P. lampas* in which the spores were just being formed. The luminescent and immature non-luminescent specimens were extracted separately and both yielded the same chemical substances.

Extracts of *P. lampas* in organic solvents gave a strongly positive Liebermann-Burchard test and a crystalline mixture of sterols was easily isolated. The mixture consisted mainly of ergosterol which commonly occurs in fungi. Another component, which has not been obtained in a pure state, lacked the characteristic ultraviolet absorption of ergosterol. Ergosteryl peroxide was presumably absent from the mixture since attempts to separate it by the chromatographic method of Wieland and Prelog (1947) were unsuccessful.

A colourless oil, consisting mainly of glycerides of oleic and saturated acids (probably palmitic and stearic), was isolated from the extracts by chromato-

* Manuscript received December 15, 1955.

† Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

graphy. It also contained a small amount of esterified sterol. The sterol was obtained after saponification of the esters so that the acid esterifying it is not known. Ergosteryl palmitate has been previously found in fungi (Wieland and Prelog 1947), but palmitic acid was only one of several produced by saponification.

The free acids extracted directly from the fungus were purified by chromatographing the methyl esters and partially separated through their urea complexes. They proved to be a mixture of long-chain saturated acids (probably stearic and palmitic) and oleic acid. The mixture of acids closely resembled that obtained by saponification of the glycerides and it seems possible that the acids were formed by the action of a lipase on the glycerides during extraction. However, the same mixture of free acids was obtained from several batches of fungus.

The water-soluble portion of the fungus contained mannitol and potassium salts of water-soluble acids. These acids are extracted from the aqueous solution only after acidification with mineral acid. Ether extraction then gave a mixture of acids which has been found by paper chromatography to have four components. Fumaric acid was easily separated by fractional crystallization and the R_f values indicated that succinic and malic acids were probably present.

It is seen that the material obtained by solvent extraction has yielded only commonly occurring substances. The luminescence may be due to compounds like the polypeptide, luciferin, isolated from the marine ostracod crustacean *Cypridina hilgendorfi* (Mann 1952; Tsuji and Harvey 1954). A search for luciferin-like substances is intended.

Experimental

Microanalyses were carried out at the C.S.I.R.O. Microanalytical Laboratory.

(a) *Extraction*.—Fresh fruiting bodies of *P. lampas* (600 g) were immersed in methanol (2 l.) and macerated. The methanol was filtered and the insoluble portion extracted again with a further 1.5 l. of hot methanol. The combined methanol extracts were concentrated under reduced pressure until most of the methanol had evaporated, leaving an aqueous solution (the fungi contain much water) and water-insoluble material which separated out. The water-insoluble material was extracted with ether and the ether extracts evaporated. By treatment with a little ethanol some sterol (0.2 g) crystallized from the crude extract. The remaining extract was separated into acidic (extracted from an ether solution by sodium carbonate) and non-acidic fractions.

(b) *Non-Acidic Fraction*.—The non-acidic part was chromatographed on alumina (activity IV). It was collected in the following fractions:

- (i) Colourless oil (3.0 g) eluted by light petroleum (b.p. 40–60 °C).
- (ii) Yellow oil (1.2 g) eluted by benzene.
- (iii) Colourless crystals (0.15 g; m.p. 143–147 °C) eluted by benzene-ether (1:1).

Fraction (i) consisted principally of glycerides (glycerol yield 9.0%) and on saponification gave a mixture of acids. In methanol these formed a urea complex from which a crystalline product (0.7 g) was obtained. It melted at 50–55 °C after recrystallization from acetone. Repeated crystallization from acetone gave a product, m.p. 55–58 °C, which showed no depression of m.p. when mixed with palmitic acid. It probably consisted of a mixture of palmitic and stearic acids (Found: C, 75.6; H, 12.8%. Calc. for $C_{15}H_{32}O_2$: C, 76.1; H, 12.7%. Calc. for $C_{18}H_{36}O_2$: C, 75.0; H, 12.5%). The oily acid (1.0 g) recovered from the mother liquors

of the urea complex was unsaturated and a test showed it was elaidinized by sodium nitrite-nitric acid. It was oxidized with performic acid by the method of Swern *et al.* (1945) and converted into *threo*-9,10-dihydroxystearic acid (m.p. 91–92 °C), which showed no m.p. depression when mixed with an authentic sample. This established the presence of oleic acid.

The yield of non-saponifiable material from fraction (i) was small. It consisted of a partly crystalline solid which was chromatographed on alumina. A trace of soft waxy solid was eluted rapidly by benzene and crystalline sterols (m.p. 145–148 °C; 0.05 g) by benzene-ether. These sterols must have been present originally as an ester, because fraction (ii) did not contain any sterol.

Fraction (ii) was also mainly fat. It gave a glycerol yield of 6.6% and like fraction (i) it gave saturated acids and oleic acid when saponified. The non-saponifiable fraction did not yield any sterol but there was some sparingly soluble (benzene, ethanol, chloroform) amorphous material which could not be crystallized.

Fraction (iii) was combined with the sterols separated from the original crude mixture and recrystallized from ethanol. Yield, 0.3–0.35 g, m.p. 146–150 °C. The recrystallized product gave a strong Liebermann-Burchard test (red→bluish black→green) and reverse Salkowski reaction. Its high negative optical rotation ($[\alpha]_D^{20} = -110^\circ$; c. 2.62 in CHCl_3) approached that of ergosterol ($[\alpha]_D^{20} = -130^\circ$). It possessed this sterol's characteristic ultraviolet absorption maxima (λ_{max} , 271, 281, 292) and by comparing the intensities at the main maxima with those recorded for pure ergosterol by Barton and Cox (1948) it is estimated that the mixture contained not more than 78–79% of ergosterol.

λ_{max}^* (m μ)	ϵ_{max}^*	$\lambda_{\text{max}}^\dagger$ (m μ)	$\epsilon_{\text{max}}^\dagger$
271	9400	271	11,900
281	9700	282	12,500

* Solution in ethanol.

† Barton and Cox (1948).

The sterols were chromatographed on alumina (activity IV) and fractions eluted by benzene and benzene-ether mixtures. Many fractions were collected and finally recombined into three almost equal fractions, according to m.p., and recrystallized from ethanol: (1) m.p. 150–155 °C; (2) m.p. 150–160 °C; (3) m.p. 161–163 °C.

Fraction (3) was practically pure ergosterol. The m.p. was undepressed by admixture with authentic ergosterol. Likewise its benzoate, m.p. 167–168 °C, showed no m.p. depression with ergosteryl benzoate (Found: C, 84.1; H, 9.9%. Calc. for $\text{C}_{28}\text{H}_{48}\text{O}_2$: C, 84.0; H, 9.7%). There was no evidence for the presence of ergosteryl peroxide which should be eluted last from the column (Wieland and Prelog 1947).

(c) *Acidic Fraction.*—The methanolic extract of the fungus also yielded a dark tarry mixture of acidic substances separated by shaking an ethereal solution with Na_2CO_3 solution. The amount of NaOH-soluble material, after removing the acids, was negligible. The crude acids were converted into methyl esters and passed through an alumina column (activity IV) in light petroleum. This gave a colourless oil, which was saponified (alc. KOH) giving acids (c. 1.3 g). These were easily separated into crystalline saturated acids, m.p. 55–57 °C (Found: C, 75.6; H, 12.6%), and oily acids, mainly oleic, by forming a urea complex. The mixed acids, before forming the urea complex, had no measurable ultraviolet absorption.

(d) *Water-Soluble Fraction.*—The solution of water-soluble material from the fungus was extracted continuously with ether. This removed a small amount of oil, with a strong "mushroom" odour, containing only a trace of acid. The aqueous solution contained 3.6 g of potassium as salts, estimated by taking a small aliquot of solution, evaporating, ashing the residue, and determining the potassium content of a solution in N/2 HCl by flame photometry.

After addition of HCl to decompose potassium salts the continuous ether extraction was repeated and crystalline acids were extracted immediately. By crystallization from a little water one of the acids was separated and identified as fumaric acid (0.5 g), m.p. and mixed m.p. 284–285 °C (sealed tube) (Found: C, 41.7; H, 3.8%. Calc. for $C_4H_4O_4$: C, 41.4; H, 3.4%).

A descending paper chromatogram on Whatman No. 1 paper, using cineole, methyl ethyl ketone, formic acid, and water as the solvent system, according to the method of Anet and Reynolds (1955), showed the presence of four acids in the mixture. The chromatogram was developed with silver nitrate in acetone. Spraying the spots with ethanolic sodium hydroxide did not cause darkening. Lack of darkening is considered to show the absence of acids having a vic-glycol or α -keto group. Four well-defined spots were obtained. Those with values for $R_F \times 100$ of 77.6, 54.0, and 26.7 are probably fumaric, succinic, and malic acids respectively. The chromatograms were run over an 18 hr period at 16 °C concurrently with authentic specimens of fumaric, succinic, and malic acids and the spots due to the authentic specimens corresponded closely to those obtained from the fungus. The fungus acids also show a further spot ($R_F \times 100 = 38.6$).

After extracting the acids the acidified aqueous solution was evaporated under reduced pressure to a thick syrup. This was extracted repeatedly with aqueous ethanol. Mannitol (2.2 g), m.p. and mixed m.p. 165–166 °C, crystallized from these extracts mixed with some potassium chloride.

(e) *Insoluble Residue*.—May and Ward (1934) show that the insoluble chitinous fraction of fungi gives glucosamine when it is heated with mineral acid. The insoluble fungal material from *P. lampas* remaining after methanol extraction was dried, powdered, and exhaustively extracted in a Soxhlet apparatus with light petroleum and chloroform in turn. This extraction removed only further small quantities of sterols and fats. A sample of the insoluble material (15 g) after solvent extraction was heated with conc. HCl and gave glucosamine hydrochloride (yield 1.0 g) (Found: C, 33.9; H, 6.4; Cl, 16.9%. Calc. for $C_6H_{14}O_5NCl$: C, 33.5; H, 6.5; Cl, 16.3%) and black insoluble material (4.7 g).

The author wishes to thank Associate Professor E. I. McLennan and Mr. J. H. Willis for examining and identifying the specimens of *P. lampas*.

References

- ANET, E. F. L. J., and REYNOLDS, T. M. (1955).—*Aust. J. Chem.* **8**: 267.
BARTON, D. H. R., and COX, J. D. (1948).—*J. Chem. Soc.* **1948**: 1357.
MANN, H. S. (1952).—*J. Amer. Chem. Soc.* **74**: 4727.
MAY, O. E., and WARD, G. E. (1934).—*J. Amer. Chem. Soc.* **56**: 1597.
SWERN, D., BILLEN, G. N., FINDLEY, T. W., and SCANLAN, J. T. (1945).—*J. Amer. Chem. Soc.* **67**: 1786.
TSUJI, F. I., and HARVEY, E. N. (1954).—*Arch. Biochem. & Biophys.* **52**: 285.
WIELAND, P., and PRELOG, V. (1947).—*Helv. Chim. Acta* **30**: 1028.

CORRIGENDUM

VOLUME 9, NUMBER 2

Page 228, 5th paragraph commencing "We are grateful to Dr. T. R. Forbes of Yale University . . ." and page 231, 5th paragraph, sentence commencing "Recently, Bloch and Tchen (1955) . . ." should be interchanged. These were added in proof on February 28, 1956.

